

Iron-catalyzed decarboxylative cross coupling reactions and palladium-catalyzed sp^2 - sp^3 coupling of coumarins.

By

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of the following thesis:

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Abstract

The thesis details the development of a decarboxylative synthesis of aryl ethers using a relatively new Iron catalyst and a novel decarboxylative coupling of coumarins catalyzed by palladium.

Aryl allyl carbonates underwent facile decarboxylative coupling in presence of a new iron catalyst. The allylation is found to be regioselective rather than regiospecific. This suggests that the allylation proceeds through π -allyl iron intermediates in contrast to related allylations of carbon nucleophiles that proceed via σ -allyl complexes. The reason we looked at iron as a catalyst was to offset the cost of expensive palladium catalyst usually used in these types of reactions.

The second project involved allyl esters of 3-carboxylcoumarins, which underwent facile decarboxylative coupling at just 25–50 °C in moderate to good yields. This represents the first extension of decarboxylative C–C bond-forming reactions to the coupling of aromatics with sp^3 -hybridized electrophiles. Finally, the same concept can be applied to the sp^2 – sp^3 couplings of pyrones and thiocoumarins. A variety of biologically important heteroaromatics can be readily functionalized without the need for strong bases or stoichiometric organometallics that are typically required for more standard cross-coupling reactions.

Acknowledgements

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For my beloved sister Ruchi and niece Rhea.

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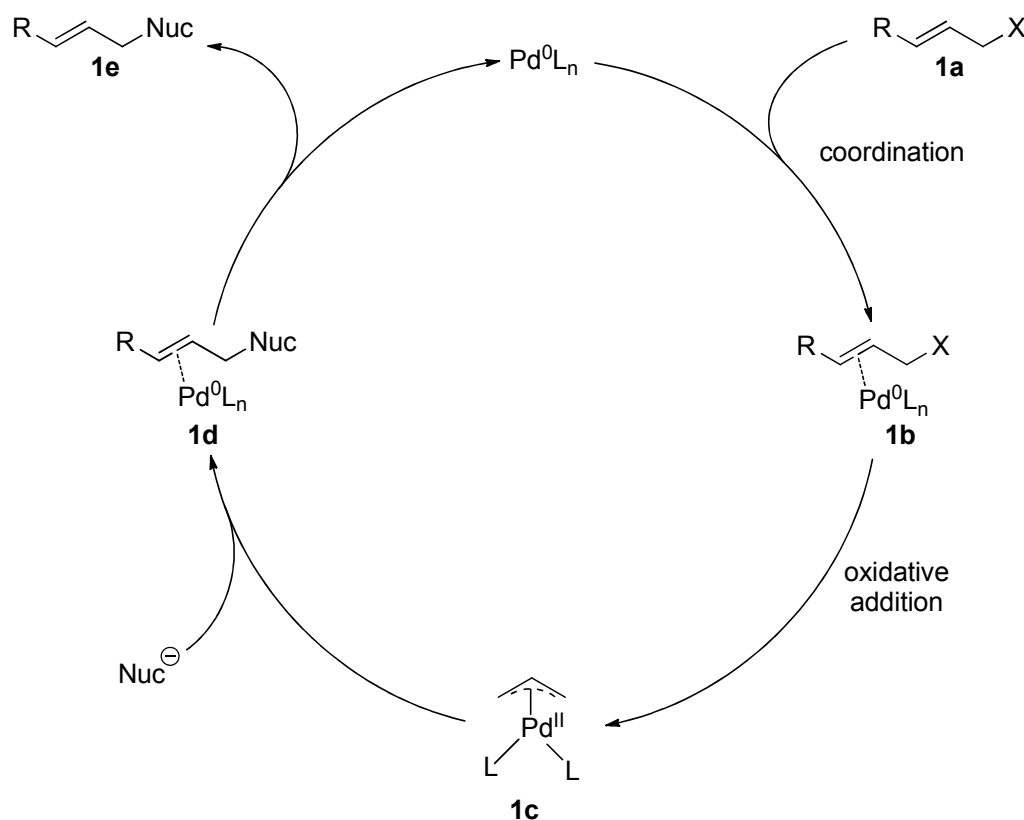
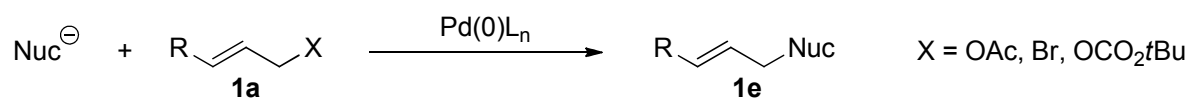
Part 1: Introduction

1.1 Allylic Etherification:

Palladium and Ruthenium-catalyzed allylation reactions have attracted a lot of attention in the last three decades. The Tsuji-Trost allylation reaction has been extensively explored and has been a source of great inspiration to many research groups since its discovery in 1965.^{1,2}

The general reaction mechanism for the Tsuji-Trost reaction is shown in Scheme 1. The first step in the reaction is co-ordination of the Pd(0) catalyst to the double bond of the allylic substrate **1a**. This is followed by the nucleophilic substitution of the leaving group (X) by the nucleophilic Pd center. As a result, the metal goes up by two oxidation states and thus this process is called an oxidative addition. The nucleophilic displacement occurs using the backbonding d-orbitals of Pd in order to generate a π -allylpalladium complex **1c**. This complex is electrophilic in nature, with the metal centre bearing most of the positive charge in case of π -allylpalladium complexes, and the three carbons of the allyl fragment share the positive charge equally amongst themselves. This complex again undergoes nucleophilic displacement by the attack of an external nucleophile in order to generate the allylated product **1e**.

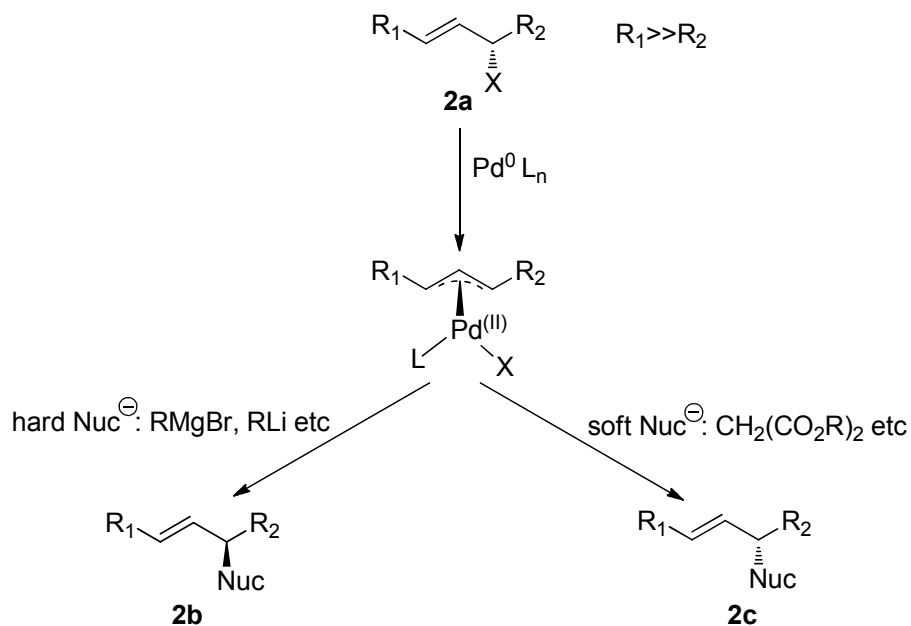
Scheme 1: Tsuji-Trost allylation reaction



Depending on the nature of the nucleophile, Trost proposed two different mechanisms³ as shown in Scheme 2. In case of hard nucleophiles, the metal center of the π -allylpalladium complex is attacked by the nucleophile, followed by reductive elimination to give the product **2b** with overall inversion of stereochemistry. Whereas, in case of soft nucleophiles, the π -allyl unit is directly attacked in a $\text{S}_{\text{N}}2$ displacement which generates the product **2c** with retention of

configuration by a double inversion mechanism. An important point to be noted here is that majority of the charge is borne on the metal centre itself, and the incoming nucleophile almost always chooses to attack the less hindered allyl carbon center purely out of steric constraints.

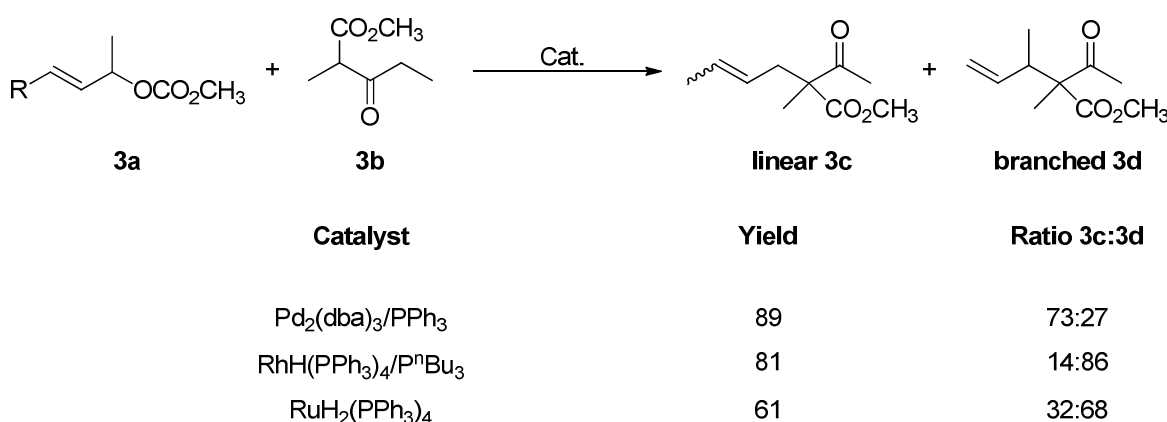
Scheme 2: Stereochemical outcomes



In case of Ru, the π -allylruthenium species **2b** has a positive charge on the metal centre. But Ru, unlike Pd, does not bear the majority of charge. Instead the charge is distributed to the terminal allyl carbons and the most substituted carbon of the allyl fragment ends up bearing majority of the positive charge. Thus, the incoming nucleophile attacks the more substituted carbon and generates the allylated product **3c** with branched selectivity. The regioselectivity is independent of the nature of the electrophile.^{3,4} Schemes 2 & 3 illustrate the

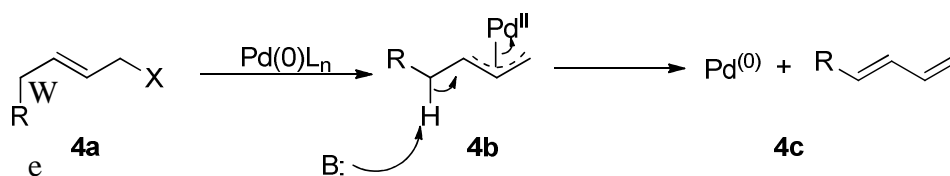
different stereochemical outcomes while using Pd and Ru centered catalysts. Tsuji reported the first ruthenium catalyzed allylic alkylation in 1985 as illustrated in Scheme 3.⁴ The branched product 3d was favored when $\text{RuH}_2(\text{PPh}_3)_4$ or a combination of $\text{RhH}(\text{PPh}_3)_4$ with n-butyl phosphine were used as catalyst. Not surprisingly, the palladium catalyst favored the formation of the linear product 3c.

Scheme 3: Ruthenium catalysis



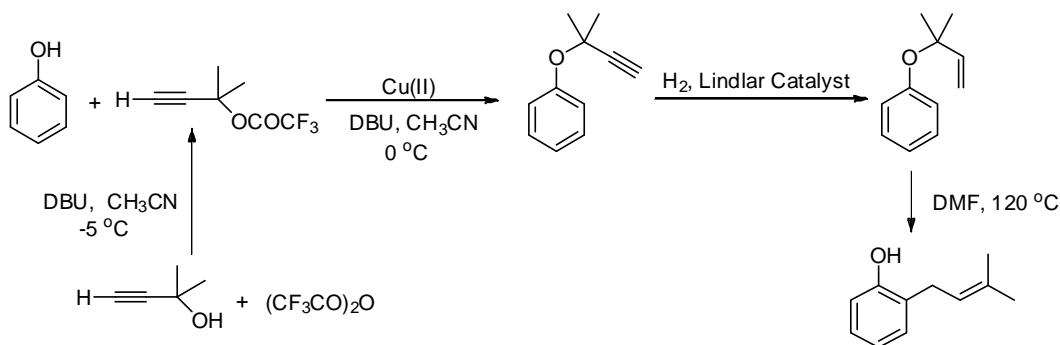
However, a major drawback with some Pd-catalyzed allylations is competing β -hydride elimination. In presence of β -hydrogens on the allyl fragment, β -hydride elimination occurs readily, giving a diene and Pd(0). Another major drawback associated with Pd and Ru-catalyzed reactions is the cost of the metal. Both Pd and Ru are very expensive metals, and it would be of great use to the industry if an economical substitute could be found for such allylation reactions.

Scheme 4: *β -hydride elimination*

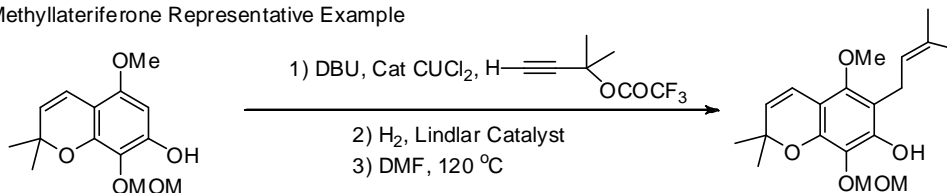


We were particularly interested in the formation of allylic ethers which could readily undergo a Claisen rearrangement in order to access prenylated phenols. In the literature, no methods exist currently that generate prenylated phenols directly from allylic carbonates. Nicolaou used a 3 step procedure, outlined in Scheme 5, to access these structures in synthesis of several natural products like lateriflorone, 1-*O*-methyllateriferone and artochamins F, H, I and J.⁵⁻⁸ The yield over these three steps is around 50-55%.

Scheme 5: *Typical prenylation procedure used by Nicolaou*

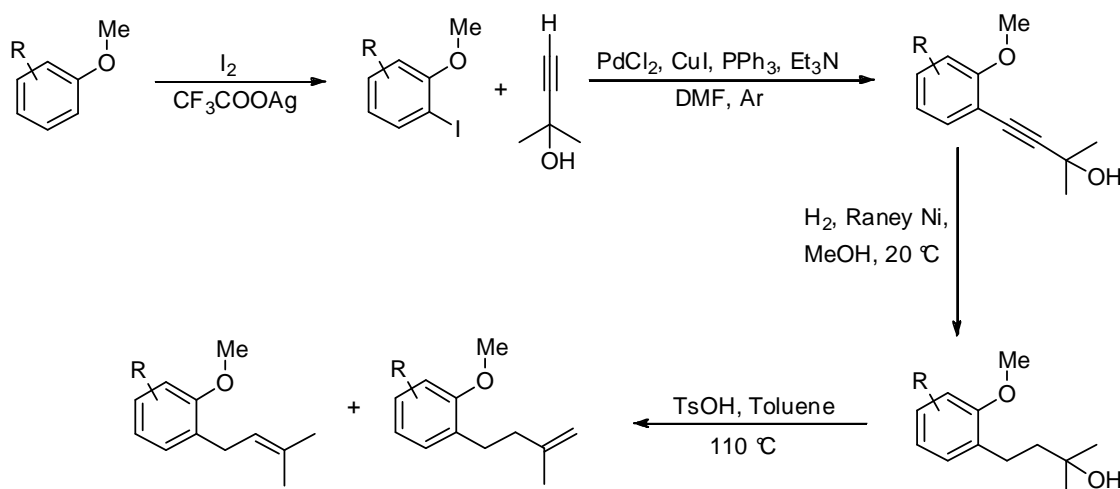


1-*O*-Methyllateriferone Representative Example



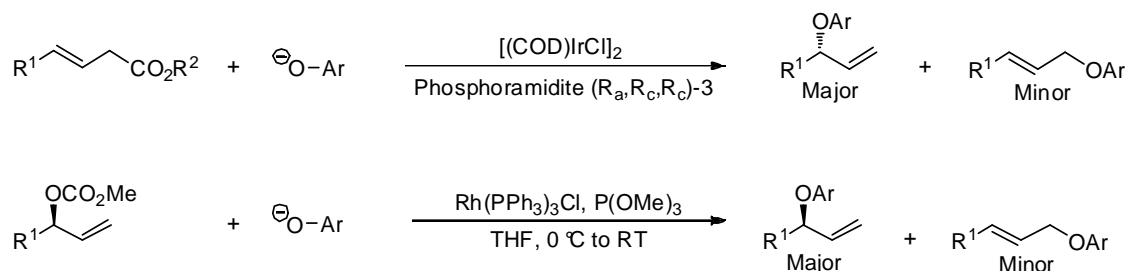
There is another report in literature by Kawamura,⁹ where traditional cross coupling methods have been used in order to access prenylated phenols (scheme 6). This particular route is quite lengthy, low yielding, and has a small substrate scope.

Scheme 6: *Cross-coupling methods*



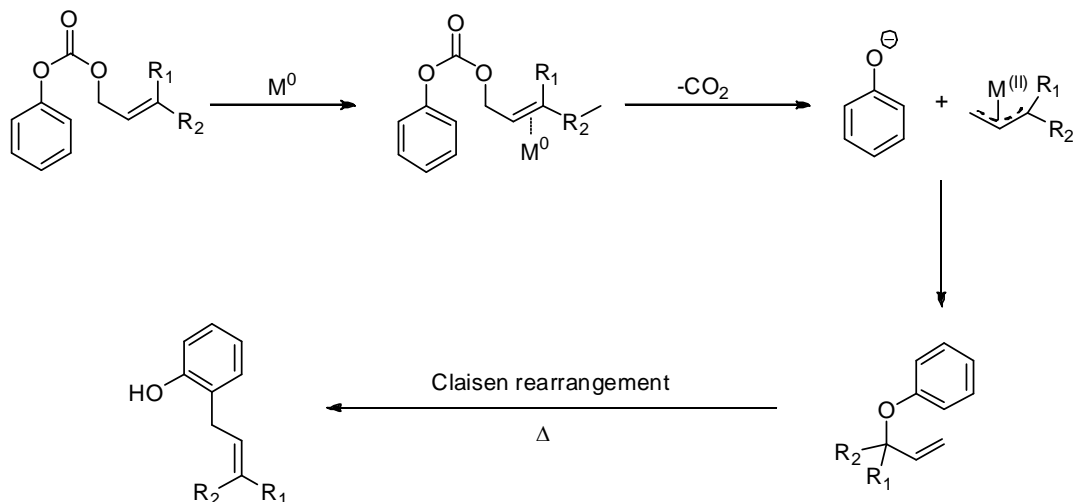
More recently, Hartwig and Evans group have come up with methods for forming substituted allylic ethers using expensive iridium and rhodium based catalysts (scheme 7).^{10, 11}

Scheme 7: *Ir and Rh catalyzed methods*



We proposed that a short concise route to access *C*-allylated phenols via an allylic etherification followed by a tandem aromatic Claisen reaction would be beneficial (Scheme 8).

Scheme 8: *Synthetic strategy*

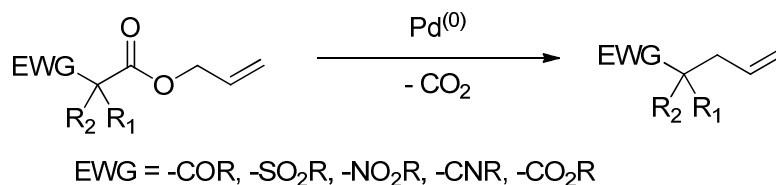


In order to get the desired phenol, we would have to generate an allylic ether *in situ* with a specific regioselectivity. To access that particular regioisomer **8a**, the incoming nucleophile after the π -allyl formation, would have to attack the more substituted carbon. This inherently requires two important things. Firstly, no β -hydride elimination should occur after π -allyl formation, and secondly, the π -allyl metal complex formed should be unsymmetrical in nature. After the formation of **8b**, we envisioned a tandem claisen rearrangement to access the phenol **8c**. A thorough literature search led us to conclude that two metals that were not reported in literature could facilitate this type of a process. In the following chapters, we discuss in detail our pursuit of this transformation.

1.2 Decarboxylative sp^2 - sp^3 coupling:

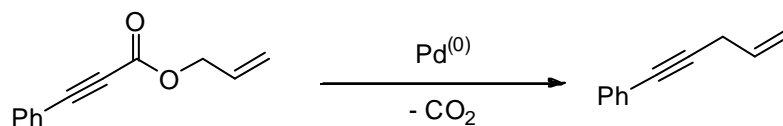
In recent years, significant effort has been devoted to the development of decarboxylative couplings that allow C—C bond forming cross-couplings without the need for preformed organometallics.¹²⁻²⁴ In avoiding the need for preformed organometallic reagents, decarboxylative couplings often avoid the use of highly basic reaction conditions¹² and the production of stoichiometric metal waste. Our group has been actively working on Pd and Ru catalyzed decarboxylative C—C bond forming reactions. Previously we have worked extensively on coupling sp^3 and sp hybridized nucleophiles with π -allylpalladium complexes.^{13, 14} In case of sp^3 -hybridized nucleophiles (Scheme 9), stabilization by an electron withdrawing group like an ester, ketone, nitro, cyano or sulfone is necessary, so as to afford a C—C coupling.¹²⁻¹⁵

Scheme 9: *Coupling of sp^3 nucleophiles*



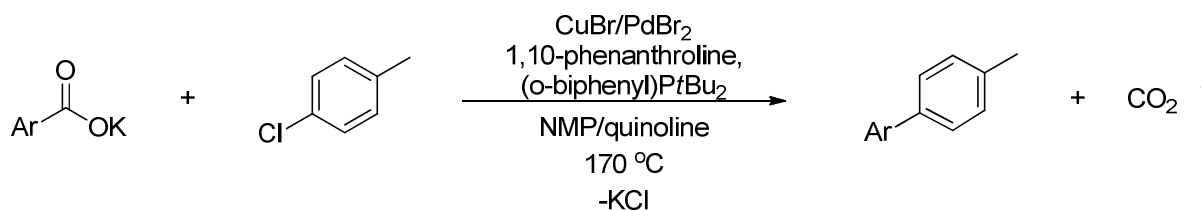
In case of sp -hybridized nucleophiles,¹³ π -allylpalladium-acetylide intermediates were accessed after decarboxylation of allyl propiolates followed by reductive elimination to give 1,4-enyne products (Scheme 10).

Scheme 10: *Coupling of sp hybridized nucleophiles*



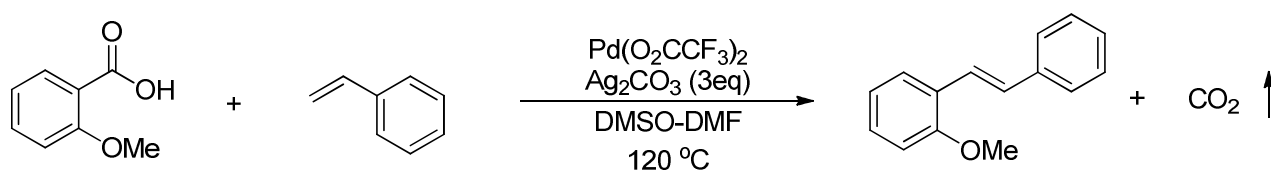
However, coupling of sp^2 -hybridized nucleophiles has been found to be particularly challenging, due to the fact that decarboxylation of a sp^2 -hybridized carboxylic acids is energetically unfavorable.¹⁶⁻¹⁹ One remarkable example is the decarboxylative biaryl synthesis developed by Gooßen (Scheme 11).^{20, 21} For all its potential utility, such sp^2 - sp^2 couplings require decarboxylative metalation of sp^2 -hybridized carbons, a relatively high energy process that utilizes copper co-catalysts at 120-170 °C. A similar, co-catalyst free, decarboxylative coupling of heteroaromatics was also reported to occur at 150 °C.²²

Scheme 11: *Biaryl coupling*



Another notable example is the coupling of aryl carboxylic acids with styrenes in presence of $Pd(II)$ and silver carbonate (Scheme 12). Major drawbacks of this reaction include the need to be heated at 120 °C and the requirement of three equivalents of expensive silver carbonate, rendering this process rather uneconomical from an industrial point of view.^{23, 24}

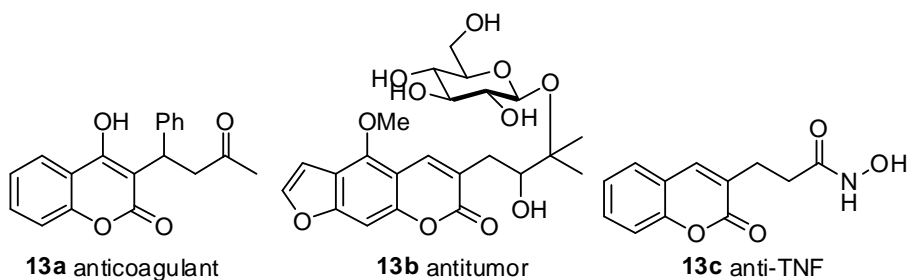
Scheme 12: Aryl acid coupling with alkenes



Thus, these promising reactions could still benefit from the development of more mild conditions for the cross-coupling. In addition, the decarboxylative coupling of aromatics and heteroaromatics has not been extended to sp^2 - sp^3 couplings, which would dramatically expand the structures that can be synthesized by decarboxylative arylation. Our initial goal was to perform a decarboxylative sp^2 - sp^3 coupling at mild to moderate temperatures. For this purpose, we investigated several molecular systems. In looking for scaffolds on which to develop decarboxylative sp^2 - sp^3 couplings, we eventually found coumarins as suitable substrates for our methodology.

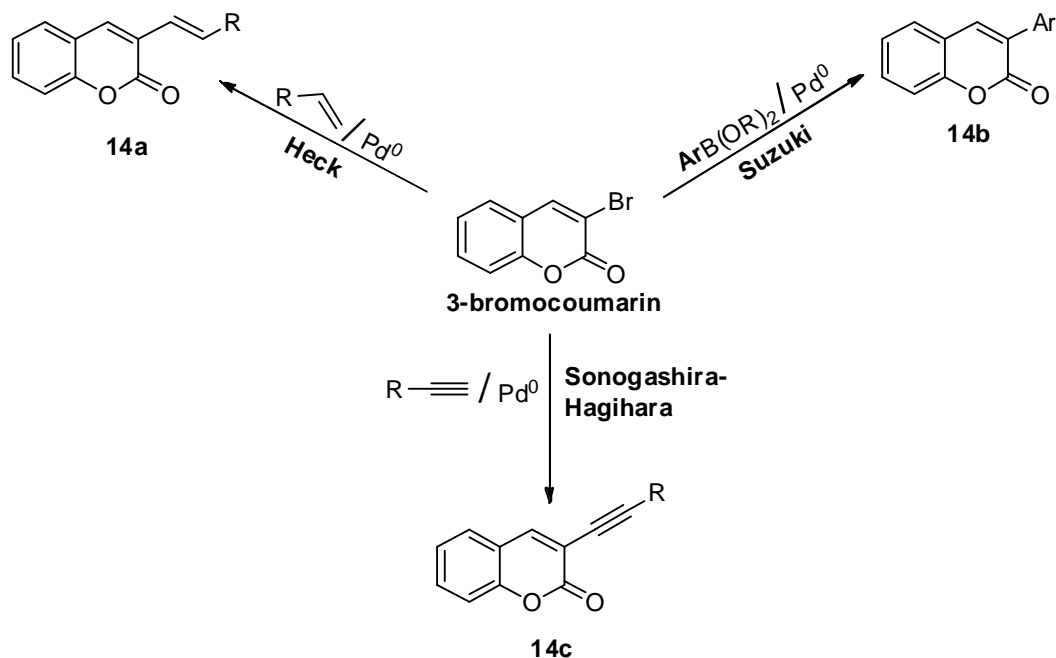
Coumarins are privileged structures in biological chemistry and numerous pharmaceuticals are based on development of this basic scaffold (Scheme 13).²⁵⁻²⁸ In principle, a decarboxylative allylation of coumarins provides access to compounds like warfarin (**13a**) and also allow the synthesis of a wide variety of 3-alkylcoumarins for biological screening. We were able to generate 3-alkyl coumarins with great ease, and filled a gap in literature with regards to the synthesis of these compounds.

Scheme 13: *Biologically active 3-alkyl coumarins*



Traditional cross coupling methods can be applied readily to 3-bromocoumarin so as to access variously substituted 3-alkyl coumarins.²⁹ As shown in Scheme 14, 3-bromocoumarin undergoes a Heck coupling to give 3-vinylsubstituted coumarin **14a**. 3-bromocoumarin can also be coupled with aryl boronic acids in a Suzuki reaction to give us 3-arylsubstituted coumarin **14b**. Lastly a Sonogashira coupling will yield acetylenic substitution at the 3 position to give **14c**.²⁹ While these standard cross-couplings are useful, a mild decarboxylative method for analogous couplings would have significant advantages like avoiding preformed organometallic reagents, basic reaction conditions and the production of stoichiometric metal waste.

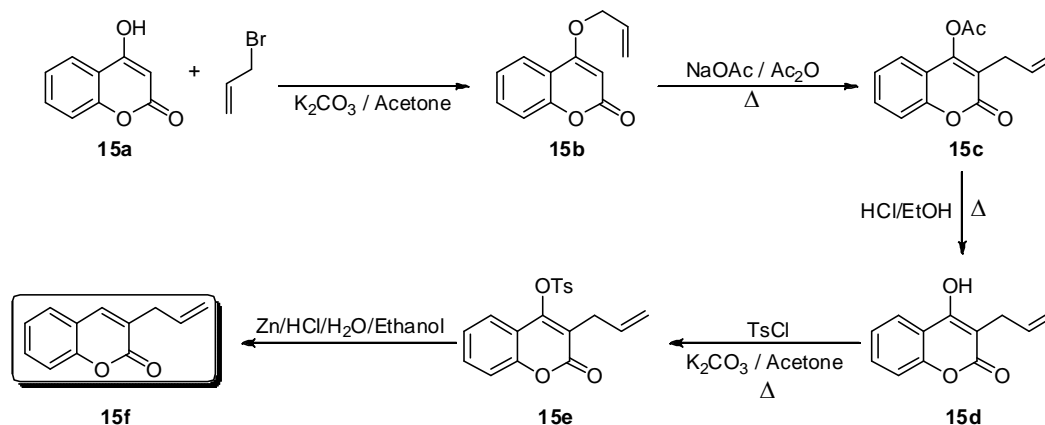
Scheme 14: Cross-coupling reactions of 3-bromocoumarin



Ahluwalia prepared 3-alkyl coumarins utilizing a Claisen rearrangement followed by a deoxygenation (Scheme 15).³⁰ In their route, they start with 4-hydroxycoumarin **15a** and form the allyl ether **15b** by reacting the former with allyl bromide in presence of a base. Heating **15b** in presence of acetic anhydride gives product **15c** as the Claisen rearranged product with an acetyl group. This is followed by a deprotection to give the free alcohol **15d**. Reaction of **15d** with tosyl chloride gives the tosylated **15e**. Treatment of **15e** with Zn/HCl in presence of water and ethanol gives product **15f** as the 3 alkyl coumarin with no substitution at the 4 position. The route gives the final product in very low yields.³⁰ As can be seen, in order to install the allyl functionality at the 3 position, the 4-hydroxy needs to be employed for a Claisen and then subsequently

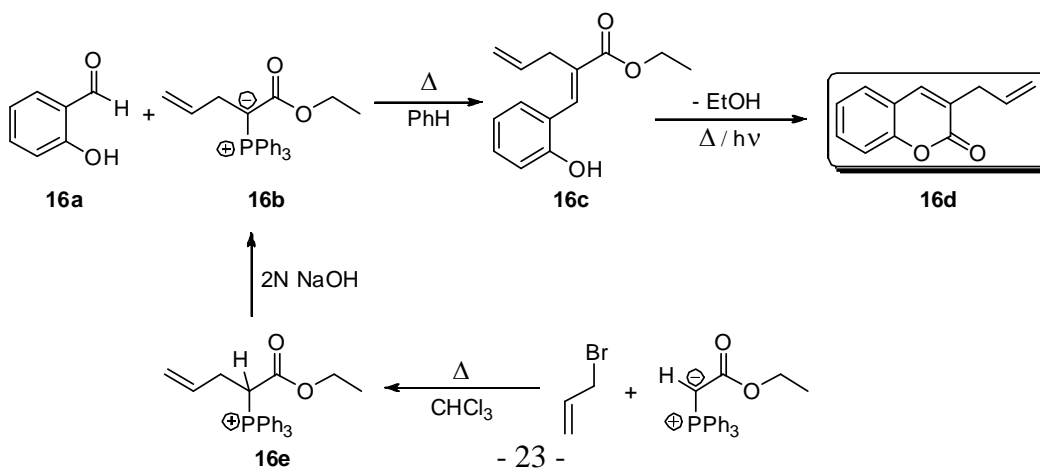
removed. These steps can be avoided if a direct coupling method was available to access 3-allyl coumarins.

Scheme 15: *Claisen route to 3-allyl coumarins*



Another way to access 3-alkyl coumarins is by forming the coumarin core from a substrate that already contains the appropriate substitution (Scheme 16).³¹ For example, the precursor to cyclization **16c**, is formed by condensing 2-hydroxy benzaldehyde **16a** with the wittig salt **16b**. The wittig salt is synthesized by simply allylating commercially available ethyl (triphenylphosphoranylidene) acetate. The diene **16c** readily undergoes cyclization with the elimination of ethanol to give 3-allyl coumarin **16d**.

Scheme 16: *Wittig methods*



As may be expected given the above illustrations, 3-alkyl coumarins have not been thoroughly utilized due to the low yielding multiple step synthetic routes required for their formation. In the following chapters we describe our methodology development and the significant advantages that our methodology possesses over the ones described above.

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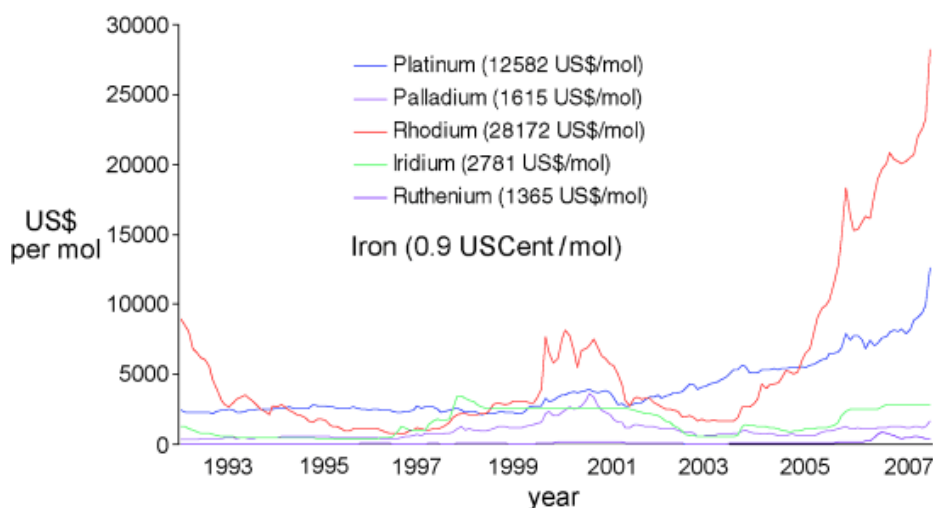
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Part 2: Regioselective Iron-Catalyzed Decarboxylative Allylic Etherification

2.1 Catalyst Selection

Our group was particularly interested in decarboxylative allylic etherification. As discussed earlier, decarboxylative allylation reactions are a powerful method for the allylation of a wide variety of nucleophiles under neutral conditions. A remaining issue with decarboxylative allylations is their reliance on relatively expensive platinum group metals.¹

Figure 1: *Cost comparison of metal catalysts*

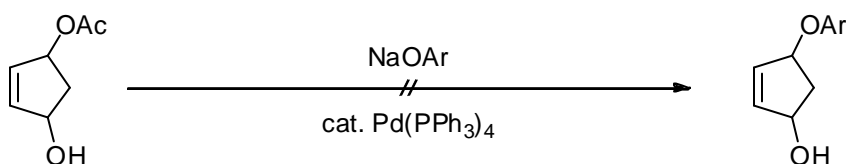


Decarboxylative allylation has been reported to occur with Pd,²⁻⁴ Rh,⁵ and more recently Ru-based catalysts.⁶⁻⁸ A single example of Nickel-catalyzed decarboxylative allylation also exists, but the yields and reaction conditions were not reported in that paper.⁵

The first palladium-catalyzed decarboxylative etherification was reported in 1981, and Larock later generalized the transformation into a useful method.⁹ Initial attempts at the intermolecular version failed, as they were not able to

catalyze the reaction of allyl acetate with phenoxides in presence of palladium (scheme 17). An intramolecular variation was reasoned to overcome reluctance of the intermolecular displacement. Initial attempts at enantioselective coupling were not fruitful (< 23% ee),⁵ however, these reactions provided the foundation for the recent enantioselective Ru-catalyzed decarboxylative etherification.⁶

Scheme 17: *Palladium catalyzed synthesis of aryl allyl ethers*



Likewise, we posited that a ruthenium centered catalyst could give us the desired regioselectivity for our transformation, but again ruthenium is also a relatively expensive metal. In search of a more economical alternative, we stumbled upon an anionic iron complex, known as the Hieber anion,¹⁰⁻¹⁸ with similar activity. We were drawn to the seminal iron-catalyzed allylic alkylations of Roustan¹⁰ and more recently Plietker.¹⁵⁻¹⁸ Roustan et al worked on catalyzing alkylations with this anionic iron complex in the early 1980's. However they were operating under an atmosphere of CO which is not desirable. We wanted to avoid CO and develop a catalytic process that operates under a more inert gas.

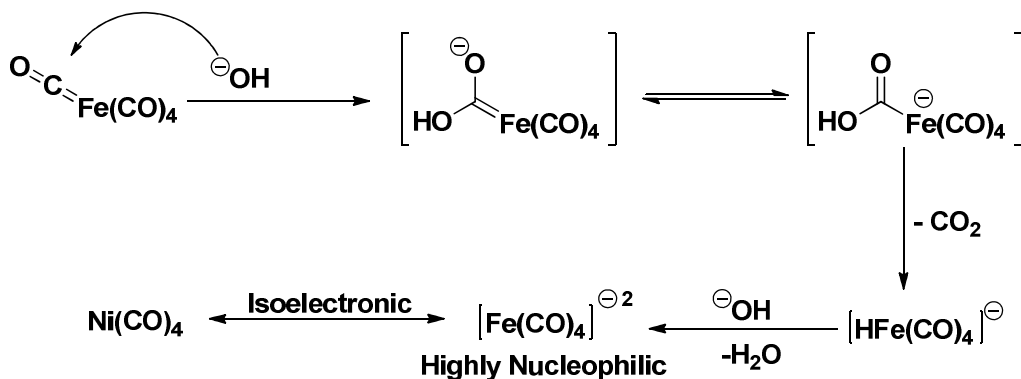
More recently, Plietker has used phosphine and *N*-heterocyclic carbene-modified versions of the Hieber anion to form electrophilic allyl species from allylic carbonates.¹⁵⁻¹⁸ However, Plietker has not investigated the loss of CO₂ from such allylic carbonates as a method for decarboxylative coupling reactions.

Thus, we chose to investigate the decarboxylative allylic etherification using this iron catalyst.

2.2 The Hieber Anion

The Hieber anion was discovered some 80 years ago by Walter Hieber. He reported the formation of nucleophilic carbonylmetalates from carbonylmetal compounds in the presence of hydroxide anions (scheme 18).¹⁹⁻²⁴ This is popularly known as the Hieber base reaction, where nucleophilic addition of hydroxide to a carbonyl ligand occurs with the subsequent loss of CO₂ and simultaneous reduction of the metal center.

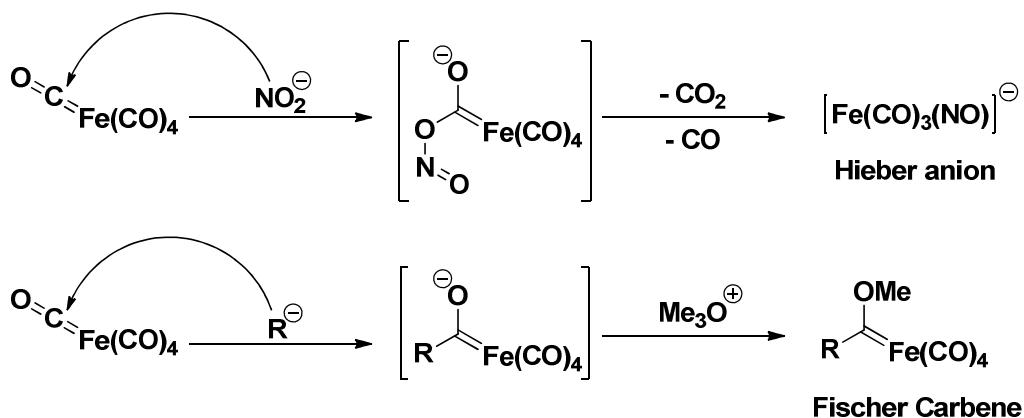
Scheme 18: *The Hieber base reaction*



The application of the Hieber base reaction to iron pentacarbonyl yields to the well-known highly nucleophilic $[\text{Fe}(\text{CO})_4]^{2-}$ dianion (Hieber anion).^{25, 26} The stoichiometric chemistry of tetracarbonyl ferrate dianion has been extensively studied.^{27, 28} In particular, the seminal contributions of Collman (Collman's reagent) demonstrated the synthetic utility of these anions.²⁹⁻³³ This anion exhibits

a high degree of electron density on the metal centre, which makes it a very strong nucleophile.²⁹ The dianion is isoelectronic with nickel tetracarbonyl, which has no nucleophilicity. Apart from hydroxide, different nucleophiles can be employed in this reaction. The use of nitrite as an oxygen centred nucleophile leads to different reaction course, in which a CO ligand is exchanged for a NO ligand with simultaneous reduction of the metal centre (scheme 19). The resulting nitrosyl complex is known as the Hieber anion and is noteworthy as it is more stable and less toxic than tetracarbonylferrate. In case carbon centered nucleophiles are used, 1, 2 addition occurs to give metallaelenolates. These can be trapped by strong alkylating reagents like Meerwein's salt to give Fischer-type carbene complexes of iron.³⁴⁻³⁶

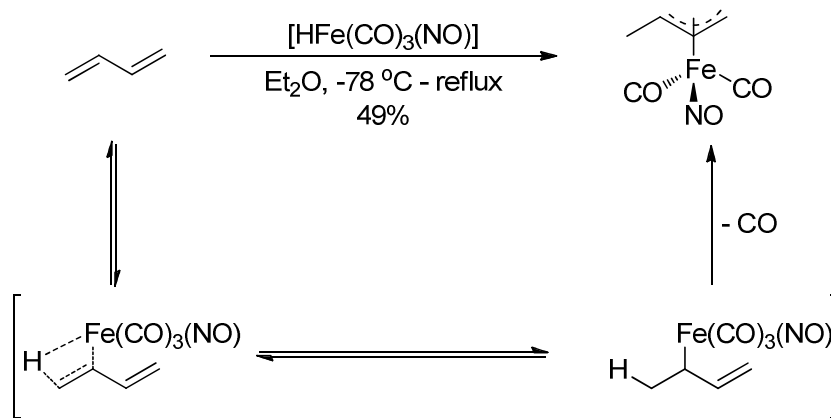
Scheme 19: *The Hieber anion*



2.3 Applications of the Hieber Anion

One of the most exciting developments with the Hieber anion was generation of stable π -allyliron complexes from dienes. This was achieved using hydridoferrate $[\text{HFe}(\text{CO})_3(\text{NO})]$ when the sodium salt of the iron complex is converted to hydridoferrate by protonation of the sodium salt with acetic or trifluoroacetic acid.³⁷⁻³⁸ Chaudhari et al reported an interesting application of the hydridoferrate complex (Scheme 20). They prepared the complex *insitu* in presence of 1,3-butadiene yielding the corresponding π -allyliron complex through hydrometallation.³⁹

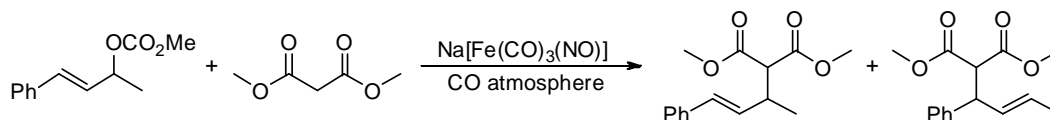
Scheme 20: π -allyliron complex



The Hieber anion has been used recently in literature by Roustan to access the π -allyliron species directly from allylic carbonates. A major drawback of this process was the need for a carbon monoxide atmosphere in order to retain catalytic activity of the complex. As seen in scheme 20, once the allyl fragment is attacked by the Hieber anion, the iron complex exchanges one of the carbon

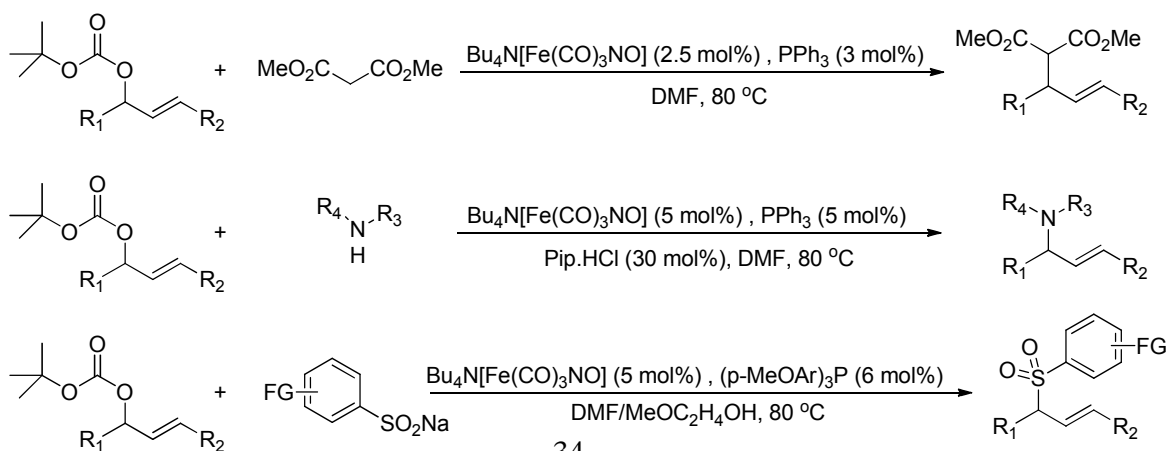
monoxide ligands for the allyl ligand. Hence after the nucleophilic substitution, the empty co-ordination site on the iron catalyst needs to be filled up by carbon monoxide.

Scheme 21: *Iron complex reactions*



More recently Plietker has used this complex to catalyze C—C bond formation. More specifically, Plietker circumvented the use of a carbon monoxide atmosphere by replacing one of the carbon monoxide ligands of $\text{NaFe}(\text{CO})_3(\text{NO})$ with a phosphine ligand. Their group has used phosphine and *N*-heterocyclic carbene-modified versions of the Hieber anion, with a tetrabutyl ammonium counterion, to form electrophilic allyl species from allylic carbonates. The reaction does not need to be run in a carbon monoxide atmosphere when phosphine or *N*-heterocyclic carbene ligands are used. This is a major advantage and makes the catalytic process very convenient. Furthermore, Plietker has also used the complex to catalyze the formation of C—S and C—N bonds.^{40, 41}

Scheme 22: *Catalytic activity of the Hieber anion*

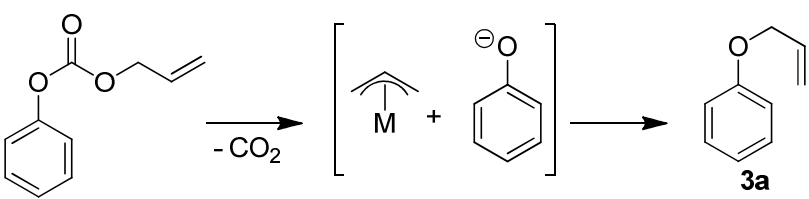


However, Plietker has not investigated the loss of CO₂ from such allylic carbonates as a method for decarboxylative coupling reactions. Thus, we chose to investigate the decarboxylative allylic etherification using iron catalysts.

2.4 Approach

To begin, we compared a small variety of catalysts for their ability to effect the decarboxylative allylation of phenols (Table 1). Here the qualitative rate of decarboxylative allylation, as catalyzed by PPh₃-modified Bu₄N[Fe(CO)₃NO] (**1**), was compared with those of more standard Pd and Ru catalysts. These studies show that the order of reactivity is Pd > Ru > Fe. While the iron catalyst was not the most active, iron is over 10,000 times less expensive than either ruthenium or palladium. Thus, the scope of the iron-catalyzed decarboxylative etherification was worthy of further investigation.

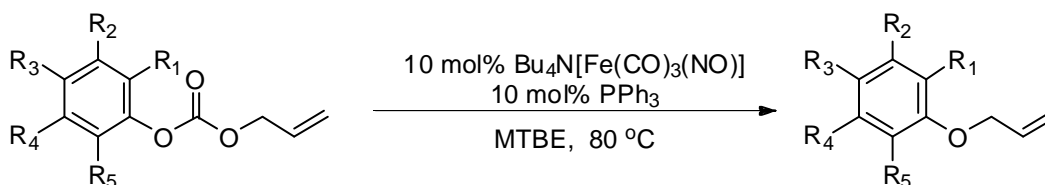
Table 1: *Catalyst comparison*

					
catalyst	solv.	temp.	time	yield	
10 mol %TBAFe, 12 mol % PPh ₃	MTBE	80 °C	24 h	98%	
1.25 mol% [Cp*RuCl] ₄ , 5 mol % bpy	DCM	50 °C	14 h	96%	
5 mol % Pd(PPh ₃) ₄	DCM	rt	<15 min.	98%	

2.5 Scope

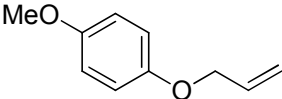
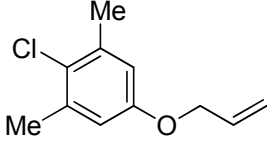
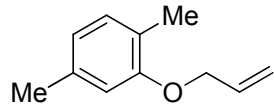
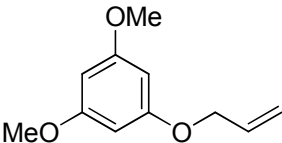
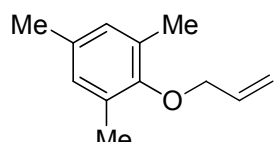
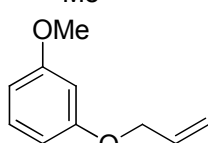
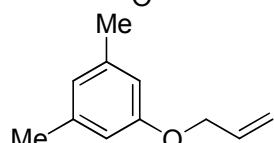
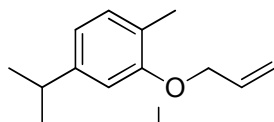
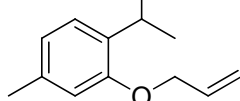
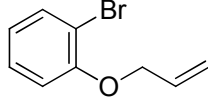
We started with simple allyl fragments, but various substitution patterns on the phenol. Decarboxylation took place at 80 °C in presence of 10 mol% of the iron catalyst. We found that triphenylphosphine was the best ligand for our reaction. The reactions were stirred in sealed vials for the time specified in Table 2 until TLC monitoring revealed there was no further increase in the ratio of product to starting material.

Scheme 23: *General reaction*



In particular, the reaction is effective for nearly any substitution pattern about the phenol; even sterically demanding phenolates undergo allylation, albeit at a reduced rate. In addition, allyl ethers of electron rich phenols like **3e** undergo exclusive *O*-allylation. Related palladium-catalyzed allylations of 3,5-dimethoxyphenol are often plagued by the formation of *C*-allylated products.^{42, 43} Lastly, aryl halides are tolerated. These functional groups have the potential to interfere with the analogous palladium-catalyzed reactions.

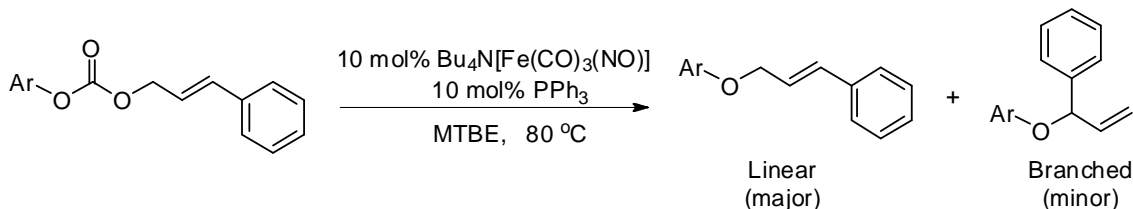
Table 2: *Decarboxylative allylation of various substituted phenols*

entry	time	product	yield (%)
1	12 h		3b 99
2	12 h		3c 92
3	12 h		3d 82
4	24 h		3e 96
5	48 h		3f 85
6	12 h		3g 92
7	24 h		3h 93
8	24 h		3i 89
9	24 h		3j 98
10	72 h		3k 85

Reaction conditions: 10 mol% Bu₄N[Fe(CO)₃NO], 10 mol % PPh₃, MTBE solvent, 80 °C

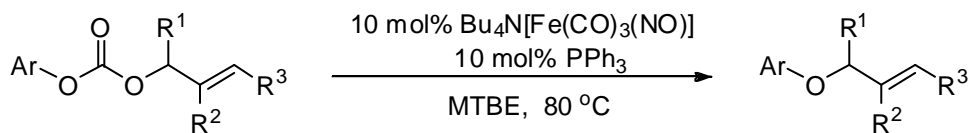
Next, the regioselectivity of the allylation was investigated (Table 3). In all cases, the cinnamyl carbonates preferentially formed the linear allylic ethers in good yield (Scheme 24).

Scheme 24: *Branched and Linear products*



Here, one can also see that the reaction is compatible with electron withdrawing groups on the phenol like CF_3 and CO_2Me . To investigate the regiospecificity of the allylation, the product of the reaction of a cinnamyl carbonate was compared to that derived from a 1-phenylallyl carbonate. As can be seen, both substrates provided the linear product exclusively as judged by ^1H NMR spectroscopy. Thus, the reaction with aryl-substituted allylic carbonates is regioselective.

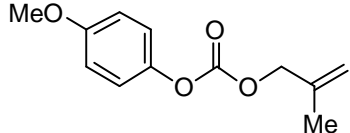
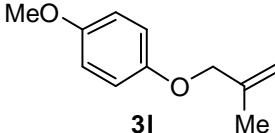
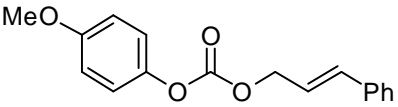
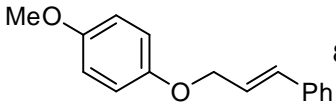
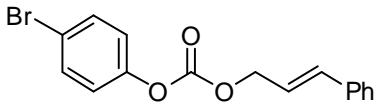
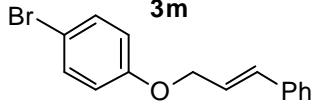
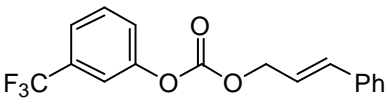
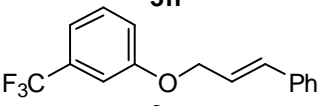
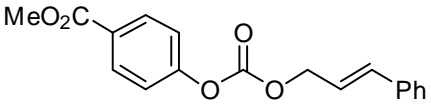
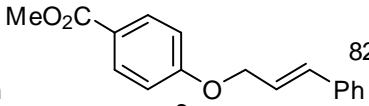
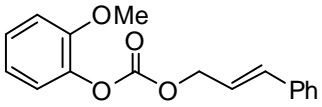
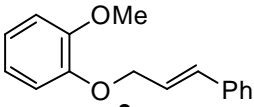
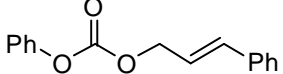
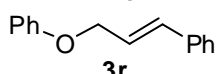
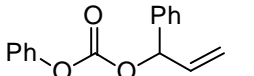
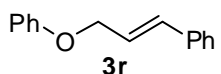
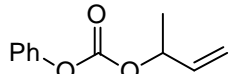
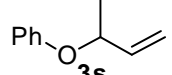
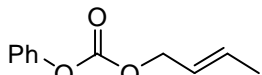
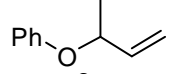
Scheme 25: *Substituted allyl fragment*



Next, we investigated the coupling of crotyl alcohol, which provided the branched allylation product with moderate regiocontrol and high yield (entry 10). The isomeric branched carbonate also produced the branched allylic ether

selectively (entry 9). While the regiochemical outcome slightly depends on the regiochemistry of the starting allyl ester, the reaction is not strongly regiospecific.

Table 3: Decarboxylative allylic etherification with substituted allyl

entry	substrate	product	yield (%) (l:b)
1		 3l	96
2		 3m	81 (>95:5)
3		 3n	83 (80:20)
4		 3o	83 (80:20)
5		 3p	82 (>95:5)
6		 3q	84 (>95:5)
7		 3r	87 (>95:5)
8		 3r	99 (>95:5)
9		 3s	95 (25:75)
10		 3s	99 (30:70)

Reaction conditions: 10 mol% Bu₄N[Fe(CO)₃NO], 10 mol % PPh₃, MTBE solvent, 80 °C

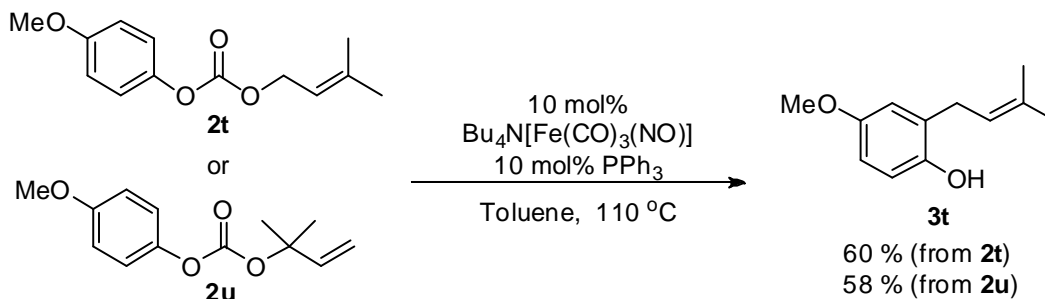
Thus, the decarboxylative etherification is best referred to as a regioselective reaction. This is an interesting observation since Xu,^{12, 13} and more recently Plietker, have shown that the analogous iron-catalyzed allylation of carbon nucleophiles is a regiospecific process, with nucleophilic attack occurring to preserve the regiochemistry present in the reactant. Thus, it appears that the iron catalyst catalyzes decarboxylative etherification through the intermediacy of π -allyl iron complexes, while allylic alkylation occurs through σ -allyl iron complexes.^{6,9}

2.6 Tandem Aromatic Claisen

Lastly, we investigated decarboxylative prenylation reactions, since prenyl aryl ethers are excellent precursors to biologically active chromans. Interestingly, the decarboxylative prenylation reaction provided the 2-prenyl phenol in moderate yield. This product may have arisen from either direct *C*-allylation of the phenolate or via a tandem *O*-allylation/Claisen rearrangement reaction. The mechanism of the transformation appears to be the latter, since direct observation of the reaction mixture reveals that the *O*-allylated product forms at intermediate reaction times and is slowly converted to the *C*-allylated product. While the yield is only moderate, our decarboxylative allylation is more straightforward than some related *C*-prenylations. For instance, Nicolaou has utilized propargylation followed by Lindlar reduction and Claisen rearrangement to control the regiochemistry of formal *C*-allylation of phenols.⁴⁴⁻⁴⁷ Lastly, it is noteworthy that attempts to utilize $\text{Pd}(\text{PPh}_3)_4$ to catalyze decarboxylative etherification of **2t** led to

quantitative elimination, forming 4-methoxyl phenol and isoprene. Thus, the iron catalyst exhibits a desirable chemoselectivity favoring substitution over elimination.

Scheme 26: *Decarboxylative prenylation*



2.7 Conclusion

In conclusion, an iron-catalyzed decarboxylative allylation of phenoxides was developed. The yields of the reaction are generally high and the iron catalyst often provides chemo- and regioselectivities that complement those of more standard palladium catalysts without any β -hydride elimination. Ultimately, the results presented herein show that decarboxylative coupling can be accomplished with iron catalysts.

2.8 Experimental

Method A: Preparation of unsubstituted allyl carbonates:

The phenol (620 mg, 5 mmol) and tetra-n-butyl ammonium chloride hydrate (9.73mg, 0.035 mmol) were dissolved in dichloromethane (5 mL) and 4M sodium hydroxide (2 mL) at 0-5 °C. Allyl chloroformate (681 mg, 5.65 mmol) was slowly added and the reaction mixture was stirred for 1 hr. After 1 hr, the two layers were separated and the organic layer was washed with 2M sodium hydroxide (5 mL) and dried over MgSO₄. A yellow oil remained after evaporation of the solvent under reduced pressure. This oil was purified by flash column chromatography using ethyl acetate and hexanes (1:10) as an eluent, (72% yield).

Method B: Preparation of substituted allyl carbonates:

A solution of alcohol (e.g. cinnamyl alcohol (642mg, 4.8 mmol)), and phenyl chloroformate (500 mg, 3.2 mmol) in dichloromethane (5 mL) was stirred for 30 minutes. A catalytic amount of dimethyl amino pyridine (DMAP, 39 mg, 0.32 mmol) and pyridine (302 mg, 3.83 mmol) were added to the reaction mixture and stirred at room temperature for 3–5 hours or until TLC showed complete consumption of starting materials. The reaction mixture was washed with 1N HCl (3 x 10 ml) and the organic layer was dried over MgSO₄. After evaporation of the solvent, the remaining yellow oil was purified by flash column chromatography with ethyl acetate and hexanes (1:10), (89% yield).

General experimental procedure for iron-catalyzed decarboxylative allylic etherification:

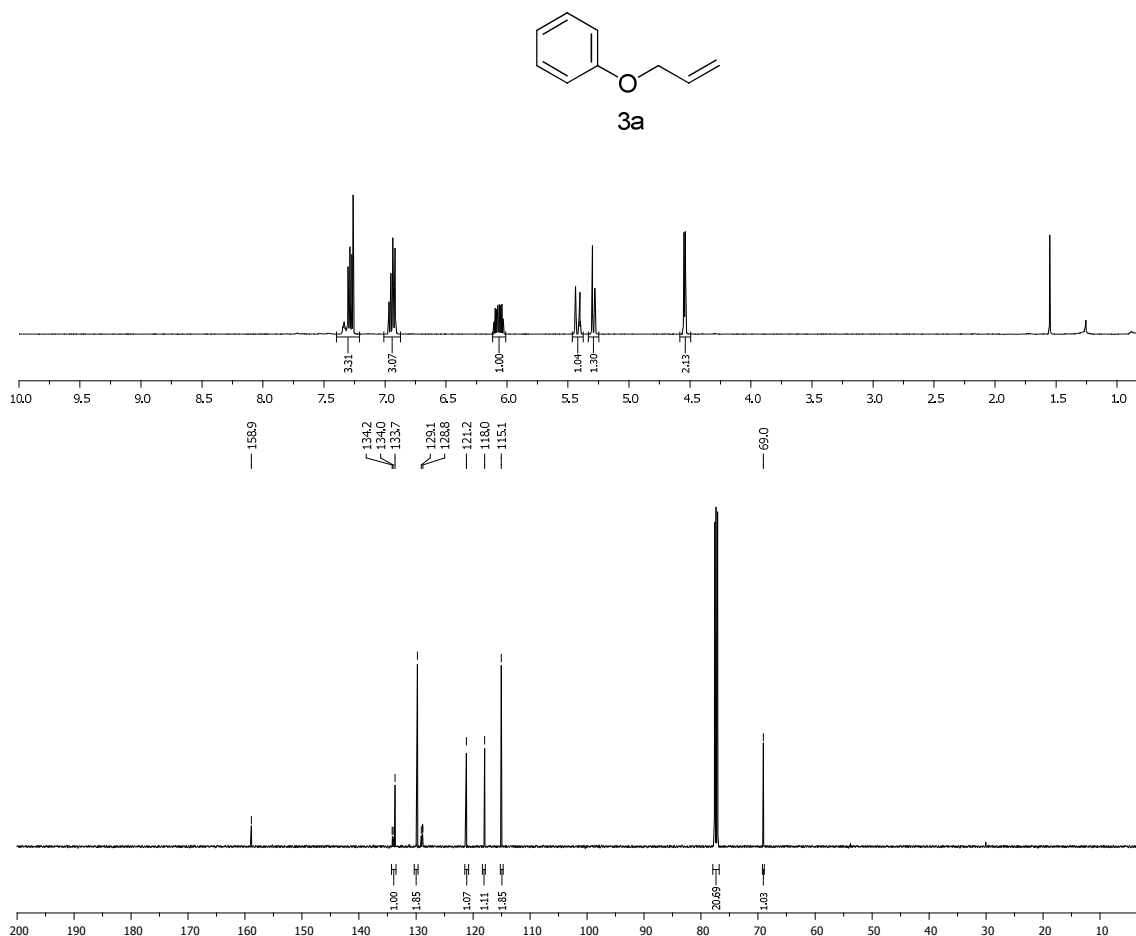
A mixture of triphenylphosphine (14.7 mg, 0.05 mmol) and $\text{Bu}_4\text{N}[\text{Fe}(\text{CO})_3(\text{NO})]$ (23.2 mg, 0.05 mmol) in methyl-*t*-butyl ether (MTBE) (2 mL) was heated at 80 °C for 30 minutes in a pressure vial with a stirring bar. After cooling to ambient temperature, the aryl allyl carbonate (0.5 mmol) was added and the vial was sealed and heated again at 80 °C until complete conversion (monitored by TLC). Purification was performed directly by column chromatography using ethyl acetate and hexanes (1:10). The products were obtained as colorless oils or white solids.

Decarboxylative allylic etherification and tandem aromatic Claisen:

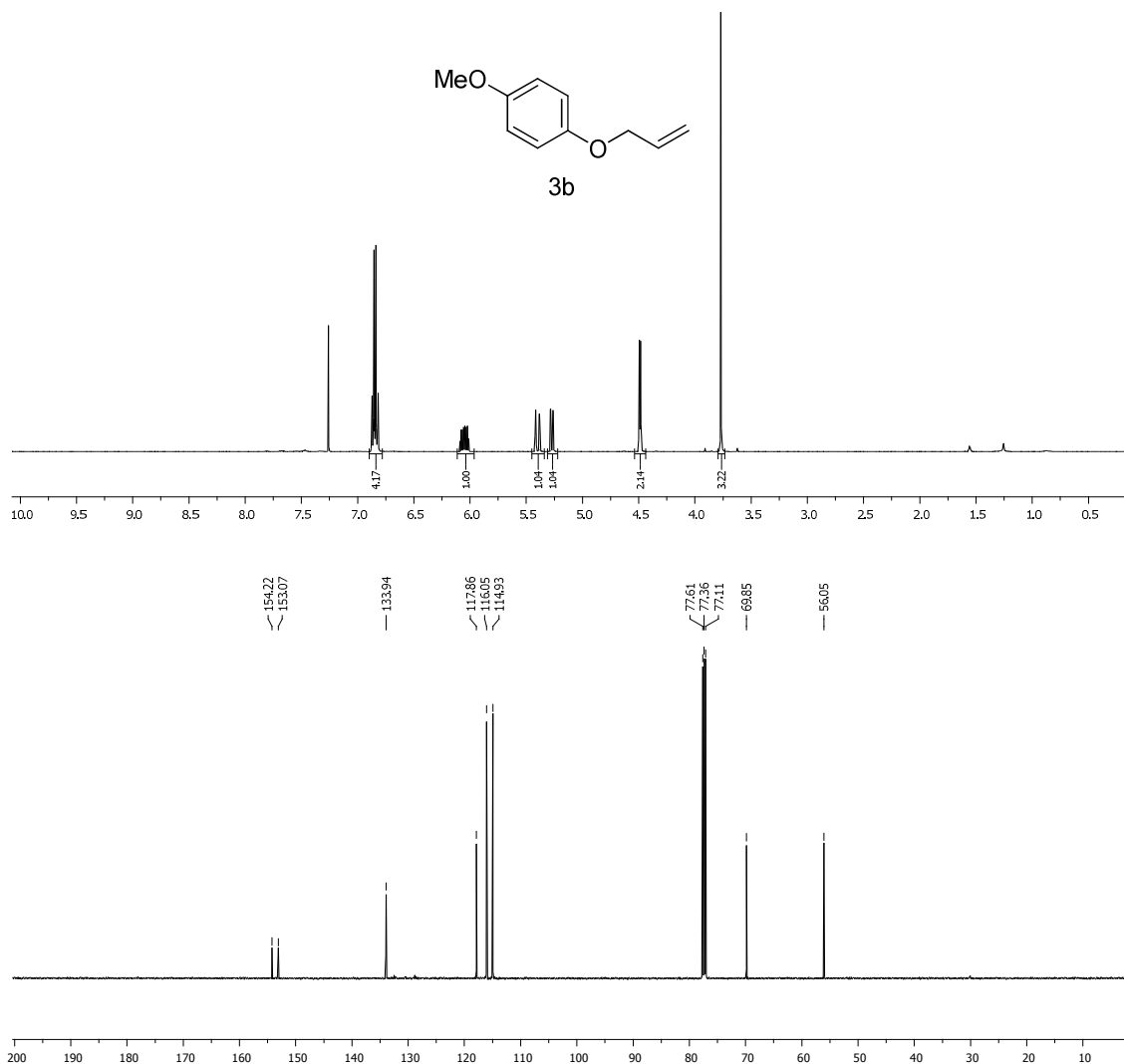
Representative procedure for 4-methoxyphenyl 3-methylbut-2-enyl carbonate:

A mixture of triphenylphosphine (11.1 mg, 0.04 mmol) and $\text{Bu}_4\text{N}[\text{Fe}(\text{CO})_3(\text{NO})]$ (17.4 mg, 0.04 mmol) in dry toluene (2 mL) was heated at 80 °C for 30 minutes in a pressure vial with a stirring bar. After cooling to ambient temperature, the 4-methoxyphenyl 3-methylbut-2-enyl carbonate (100mg, 0.423 mmol) was added and the vial was sealed and heated again at 110 °C until complete conversion was evident (monitored by TLC). The solvent was removed under reduced pressure and the crude product was subjected to column

chromatography using ethyl acetate and hexanes (1:10). The product was obtained as colorless oil.

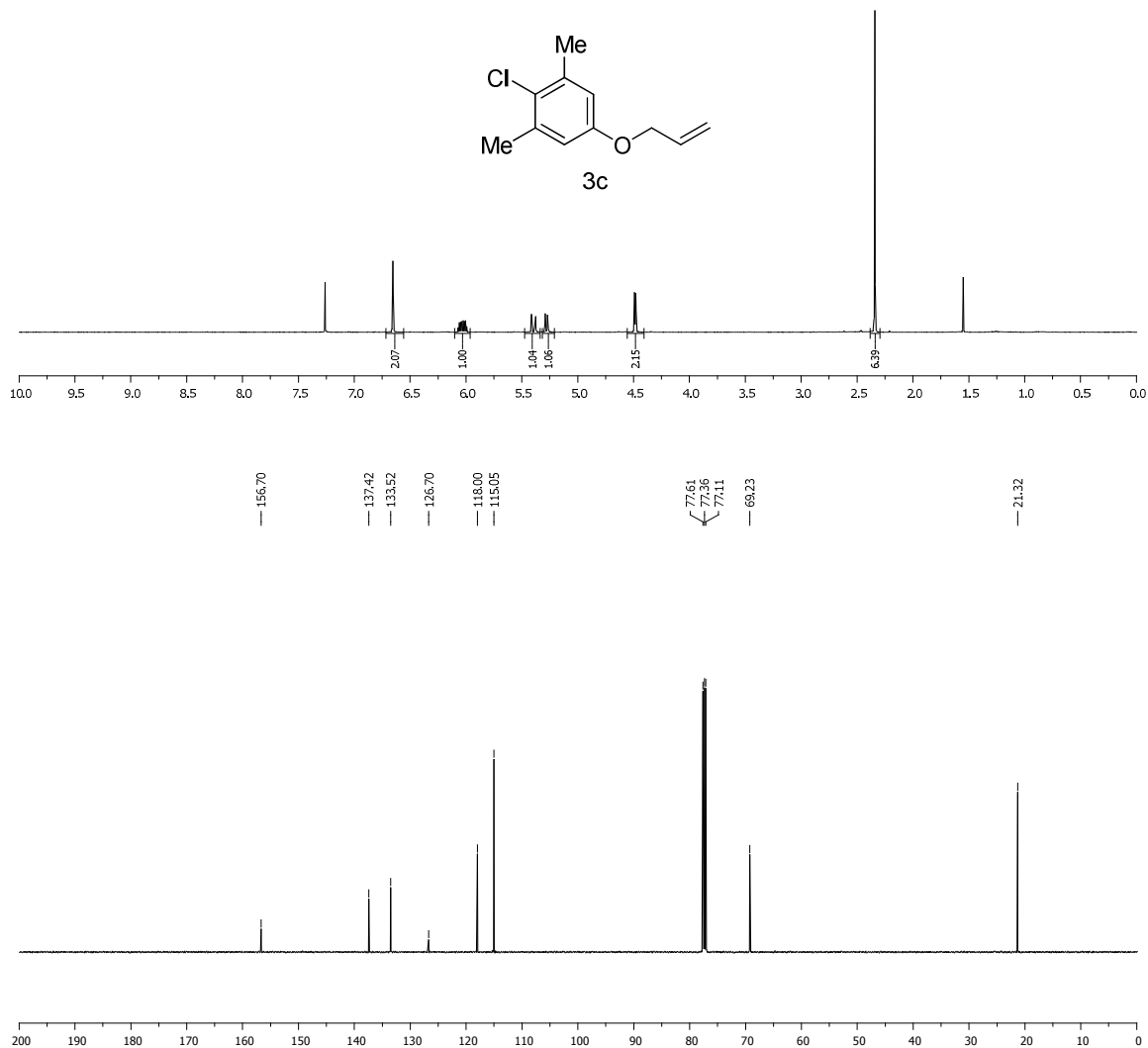


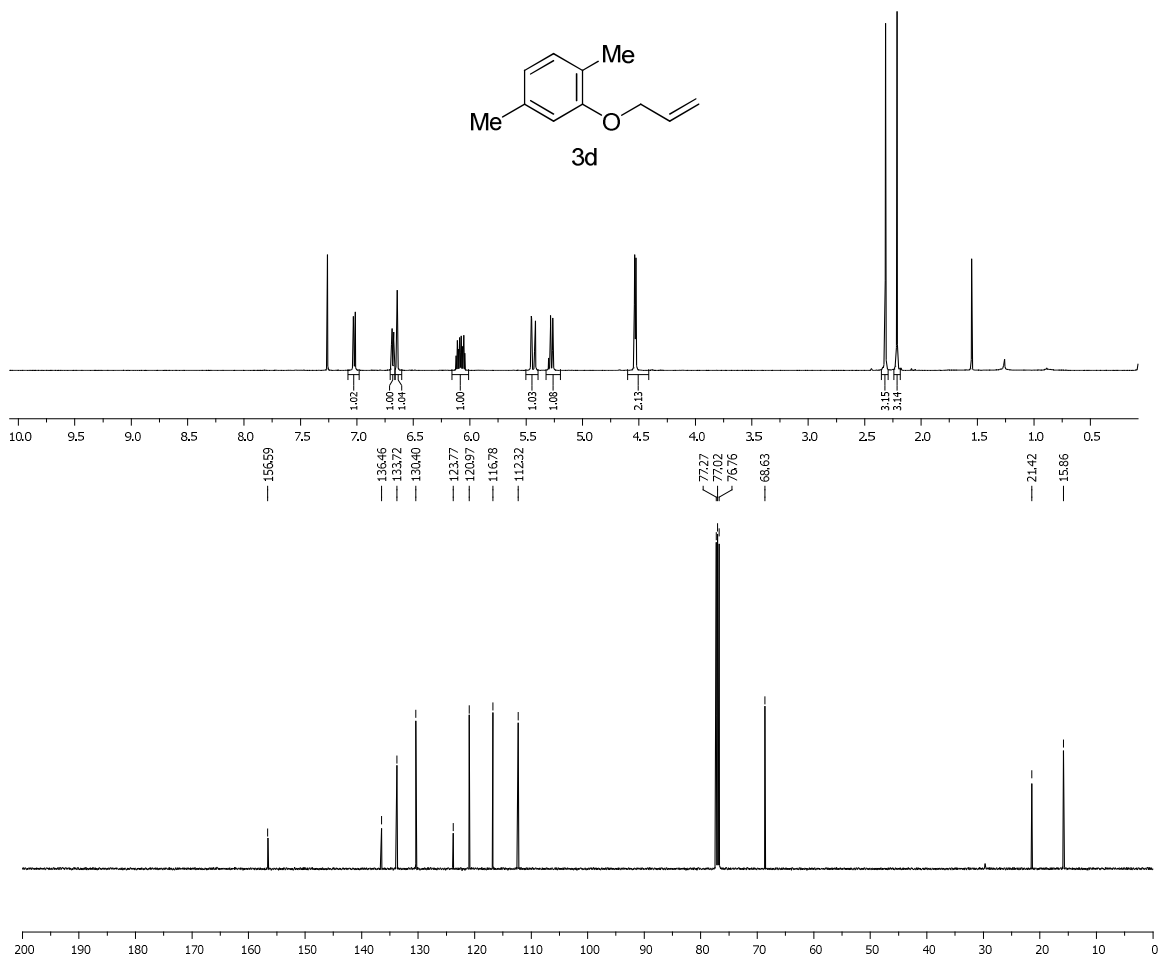
¹ Satoh T., Ikeda M., Miura M., Nomura M., *J. Org. Chem.*, **1997**, 62, 4877 – 4879.



3b: 1-(allyloxy)-4-methoxybenzene:² Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 6.90 – 6.78 (m, 4H:ArH), 6.09–6.01 (m, 1H:CH=CH₂), 5.40 (d, *J* = 17.3, 1H_E:CH=CH₂), 5.27 (d, *J* = 10.5, 1H_Z:CH=CH₂), 4.49 (d, *J* = 5.3, 2H:CH₂-CH=), 3.77 (s, 3H:O-CH₃). ¹³C NMR (126 MHz, CDCl₃) δ 154.2 (Quat, ArC-OMe), 153.0 (Quat, ArC-O-CH₂), 133.9 (CH=CH₂), 117.8 (CH=CH₂), 116.0 & 114.9 (ArCH), 69.8 (O-CH₂-CH=), 56.0 (CH₃-OAr). ν_{max} 1508, 1230, 1039, 478, 459, 447 cm⁻¹.

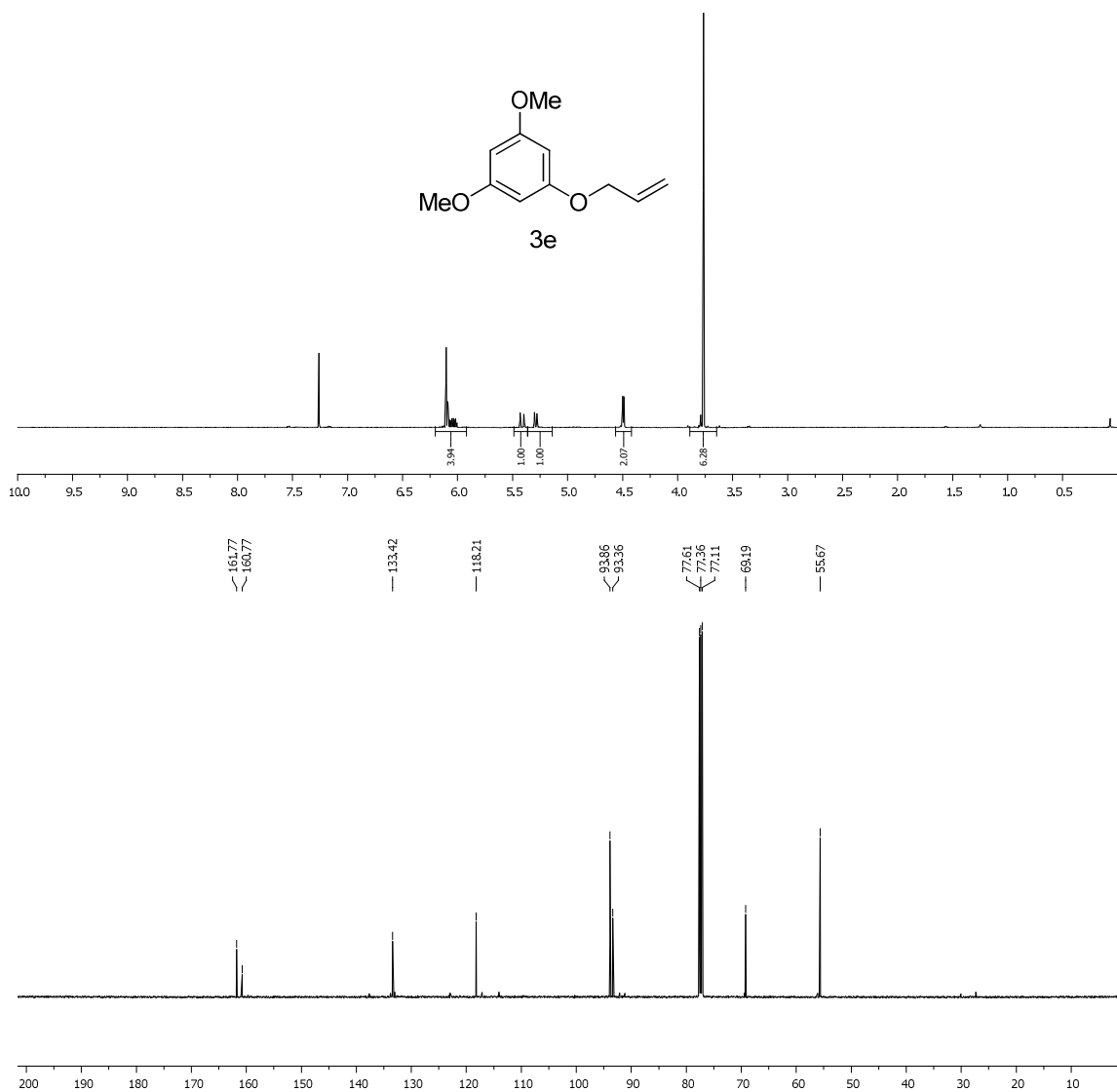
² Jimenez-Gonzalez, L., Alvarez-Corral, M., Munoz-Dorado, M., Rodriguez-Garcia, I., *Chem. Comm.*, **2005**, 7, 933 – 935.



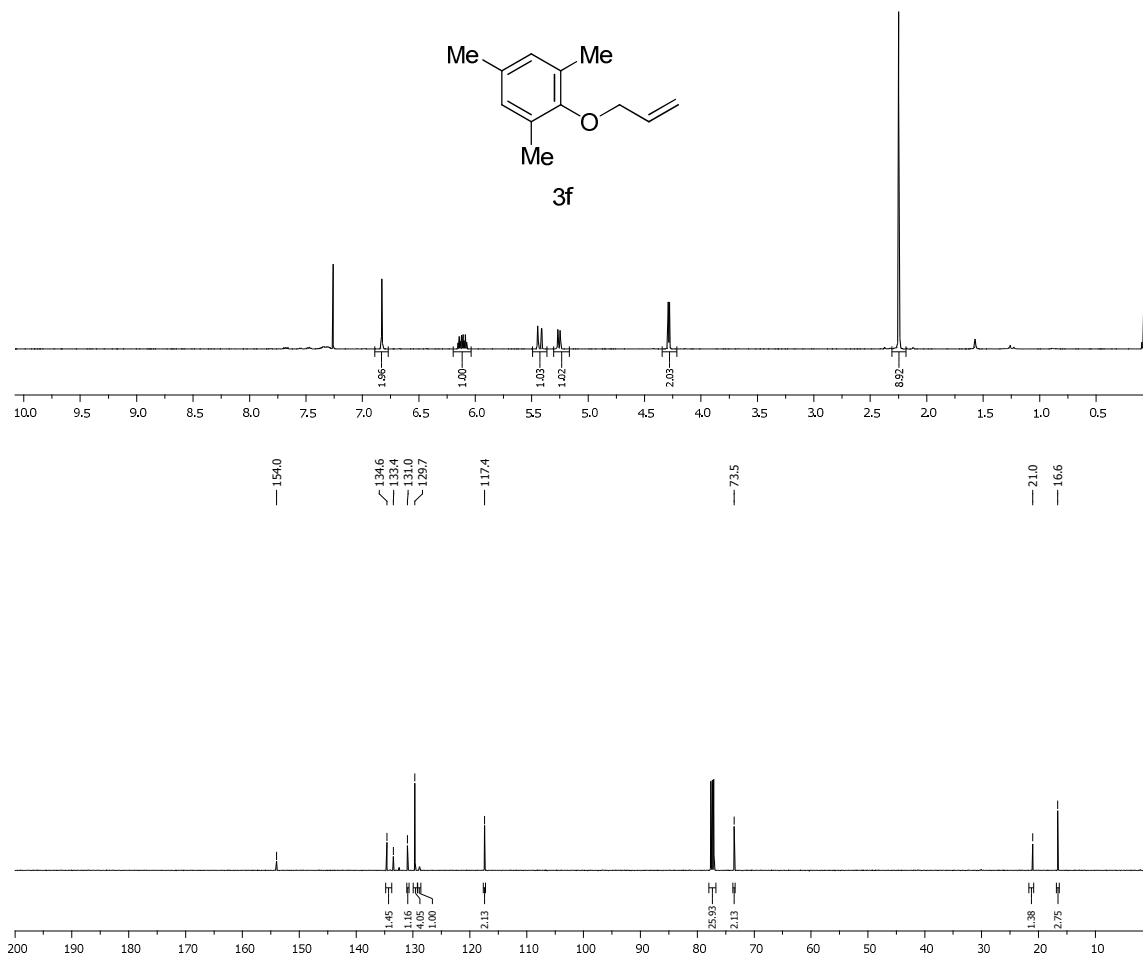


3d: 2-(allyloxy)-1,4-dimethylbenzene.³ Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 7.02 (d, *J* = 7.4, 1H:2-ArH), 6.68 (d, *J* = 7.5, 1H:5-ArH), 6.64 (s, 1H:3-ArH), 6.16 – 6.01 (m, 1H:CH=CH₂), 5.44 (d, *J* = 17.3, 1H_E:CH=CH₂), 5.27 (d, *J* = 10.6, 1H_Z:CH=CH₂), 4.53 (d, *J* = 5.0, 2H:CH₂-CH=), 2.32 (s, 3H:4-CH₃-Ar), 2.21 (s, 3H: 3H:2-CH₃-Ar). ¹³C NMR (126 MHz, CDCl₃) δ 156.5 (Quat., ArC-O), 136.4 (Quat, Ar 4-C-CH₃), 133.7 (CH=CH₂), 130.4 (ArCH), 123.7 (Quat, Ar 1-C-CH₃), 120.9 (ArCH), 116.7 (CH=CH₂), 112.3 (ArCH), 68.6 (O-CH₂-CH=), 21.4 (4-CH₃-Ar), 15.8 (1-CH₃-Ar). ν_{max} 3996, 3197, 3147, 2999, 1560, 1431, 459 cm⁻¹.

³ Petit, P., Bourgeois, P., *J.Chem. Res.*, **2004**, 3, 194 – 195.

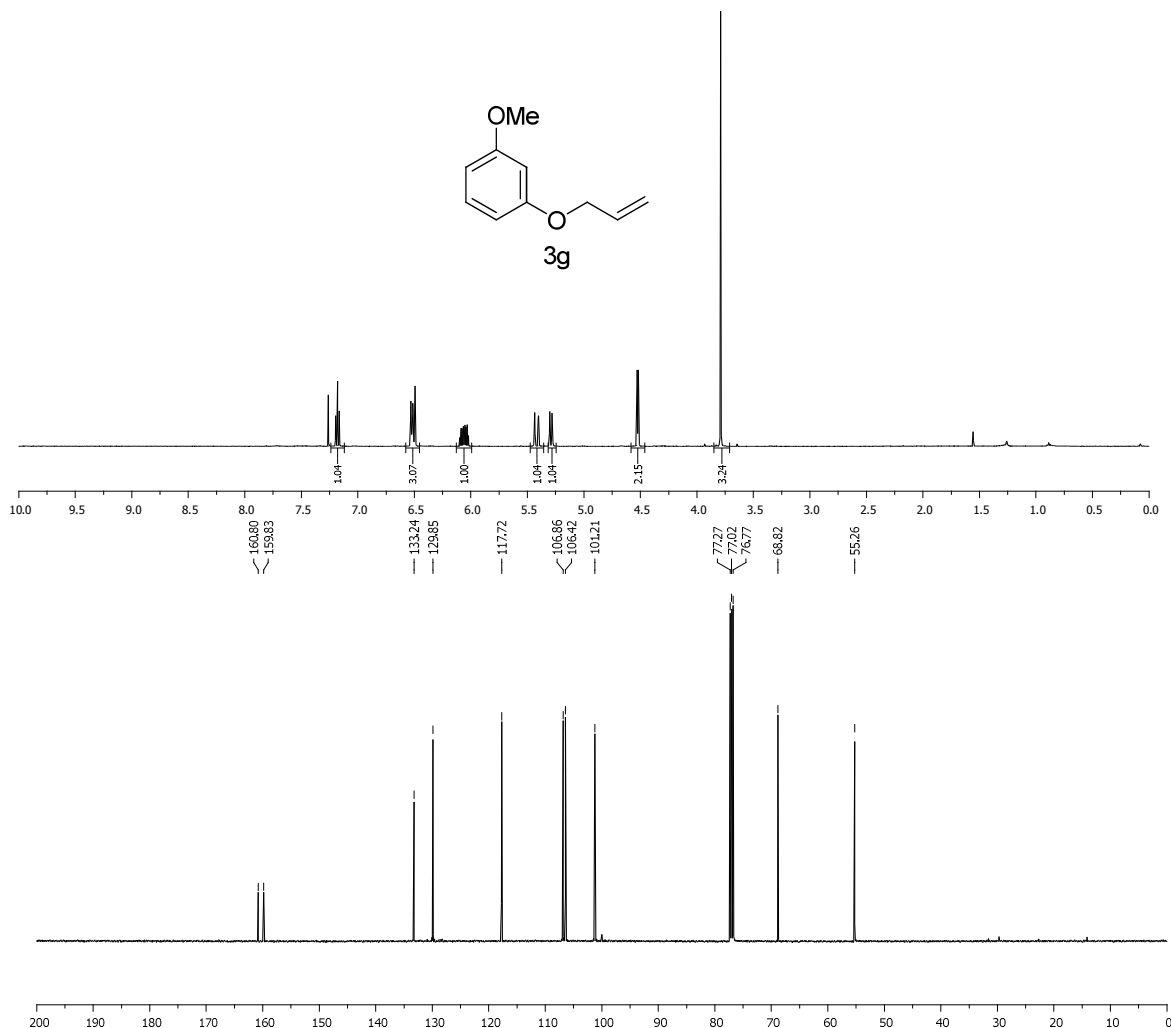


3e: 1-(allyloxy)-3, 5-dimethoxybenzene: Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 6.20 – 5.92 (m, 4H: 3ArH overlapping 1CH=CH₂), 5.41 (d, *J* = 17.2, 1H_E:CH=CH₂), 5.29 (d, *J* = 10.5, 1H_Z:CH=CH₂), 4.49 (d, *J* = 5.3, 2H:CH₂-CH=), 3.77 (s, 6H:O-CH₃). ¹³C NMR (126 MHz, CDCl₃) δ 161.7 (Quat, ArC-OMe), 160.7 (Quat, ArC-O-CH₂), 133.4 (CH=CH₂), 118.2 (CH=CH₂), 93.8 & 93.3 (ArCH), 101.2 (ArCH), 69.9 (O-CH₂-CH=), 55.6 (CH₃-OAr). v_{max} 1598, 1205, 1151, 1064, 929, 817 cm⁻¹; HRMS calcd. for C₁₁H₁₄O₃ (M+Li) 201.1103; found 201.1111.



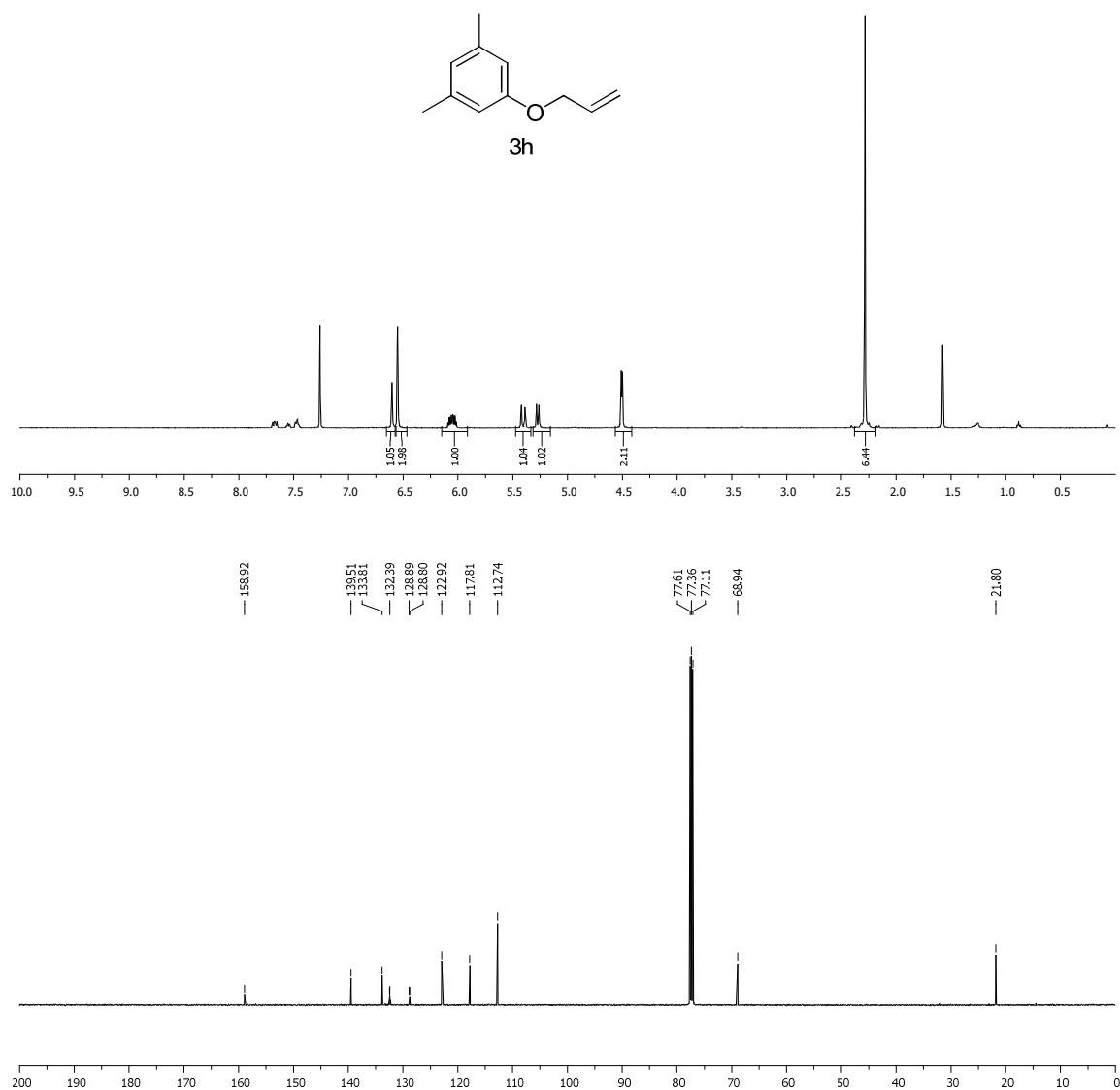
3f: 2-(allyloxy)-1, 3, 5-trimethylbenzene:⁴ Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 6.83 (s, 2H: ArH), 6.20 – 6.04 (m, 1H:CH=CH₂), 5.43 (d, *J* = 17.2, 1H_E:CH=CH₂), 5.26 (d, *J* = 10.4, 1H_Z:CH=CH₂), 4.28 (d, *J* = 5.6, 2H:CH₂-CH=), 2.25 (s, 9H: 2, 4 & 6-CH₃-Ar). ¹³C NMR (126 MHz, CDCl₃) δ 154.0 (Quat., ArC-O), 134.6 (Ar-CH), 133.4 (CH=CH₂), 130.9 (Quat, 4-ArC-Me), 129.6 (2,6-ArC-Me), 117.4 (CH=CH₂), 73.5 (O-CH₂-CH=), 21.0 (4-CH₃-Ar) 16.6 (2 & 6-CH₃-Ar). δ 154.01, 134.59, 133.44, 130.96, 129.67, 117.41, 73.51, 21.01, 16.62. ν_{max} 1934, 1483, 1458, 1307, 1261, 1213, 1147, 1035, 696 cm⁻¹.

⁴ Satoh T., Ikeda M., Miura M., Nomura M., *J. Org. Chem.*, **1997**, 62, 4877 – 4879.



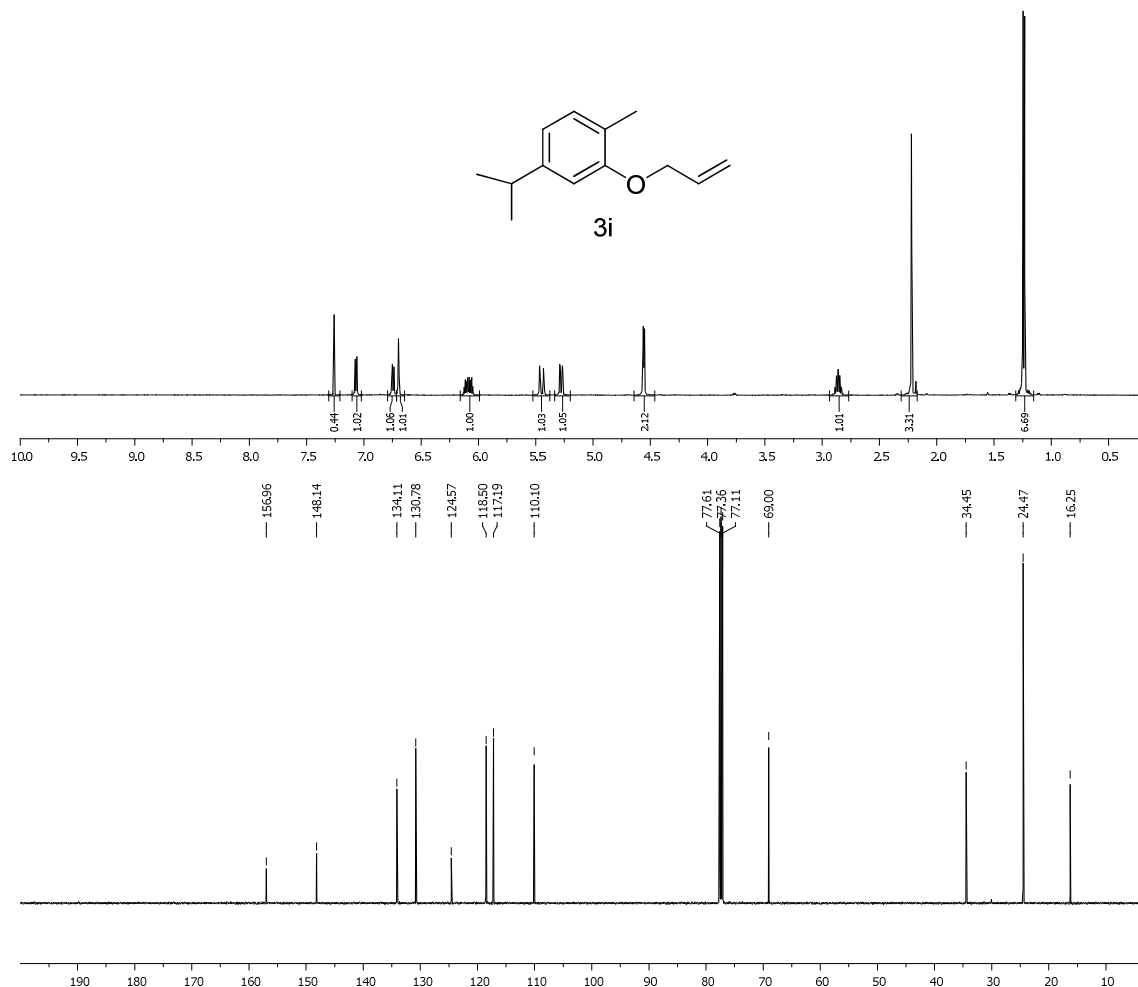
3g: 1-(allyloxy)-3-methoxybenzene:⁵ Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 7.18 (t, *J* = 8.2, 1H: ArH), 6.58 – 6.45 (m, 3H:ArH), 6.13 – 5.99 (m, 1H:CH=CH₂), 5.42 (d, *J* = 17.3, 1H_E:CH=CH₂), 5.29 (d, *J* = 10.5, 1H_Z:CH=CH₂), 4.52 (d, *J* = 5.3, 2H:CH₂-CH=), 3.79 (s, 3H:O-CH₃). ¹³C NMR (126 MHz, CDCl₃) δ 160.8 (Quat, ArC-OMe), 159.8 (Quat, ArC-O-CH₂), 133.2 (CH=CH₂), 129.8 (ArCH) 117.7 (CH=CH₂), 106.8 & 106.4 (ArCH), 101.2 (ArCH), 68.82 (O-CH₂-CH=), 55.26 (CH₃-OAr). ν_{max} 2840, 1593, 1454, 1434, 1288, 1259, 1118, 1093, 1043, 748, 696, 541, 503 cm⁻¹.

⁵ Gozzo, F. C., Fernandes, S. A., Rodrigues, D., Eberlin, M., Marsaioli, A. J., *J. Org. Chem.*, **2003**, 68, 5493 – 5499.



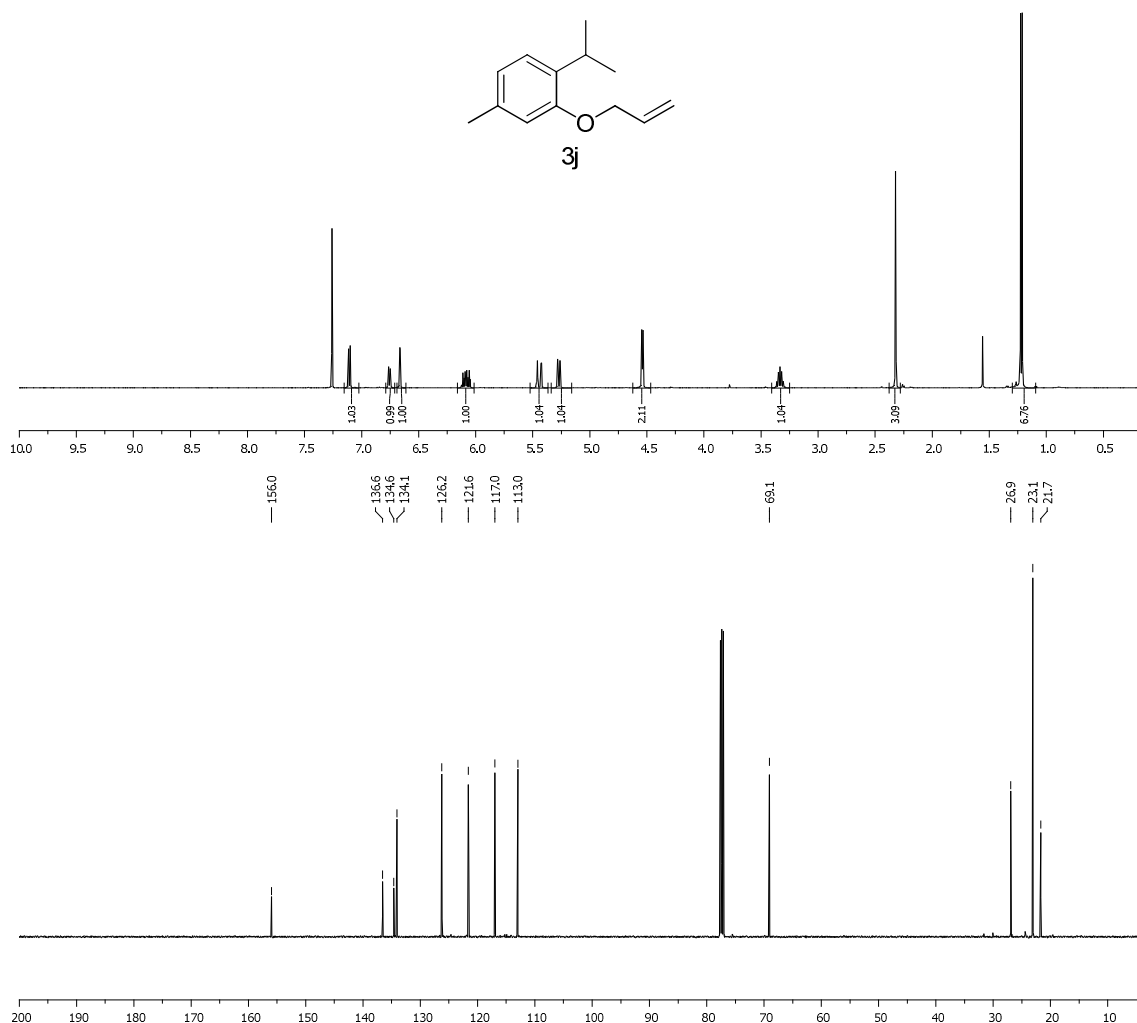
3h: 1-(allyloxy)-3, 5-dimethylbenzene:⁶ Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 6.60 (s, 1H:ArH), 6.55 (s, 2H:ArH), 6.15 – 5.91 (m, 1H:CH=CH₂), 5.40 (d, *J* = 17.3, 1H_E:CH=CH₂), 5.27 (d, *J* = 10.5, 1H_Z:CH=CH₂), 4.50 (d, *J* = 5.3, 2H:CH₂-CH=), 2.28 (s, 6H: 2& 4-CH₃-Ar). ¹³C NMR (126 MHz, CDCl₃) δ 158.9 (Quat., ArC-O), 139.5 (Quat, Ar 3 C-CH₃), 133.8 (CH=CH₂), 132.4 (ArCH), 122.9 (ArCH) 117.8 (CH=CH₂), 112.7 (ArCH), 68.9 (O-CH₂-CH=), 21.4 (CH₃-Ar). v_{max} 2918, 1595, 1170, 1155, 991, 925 cm⁻¹.

⁶ Won Y., Im E., *Org. Lett.*, **2005**, 7, 3355–3358.

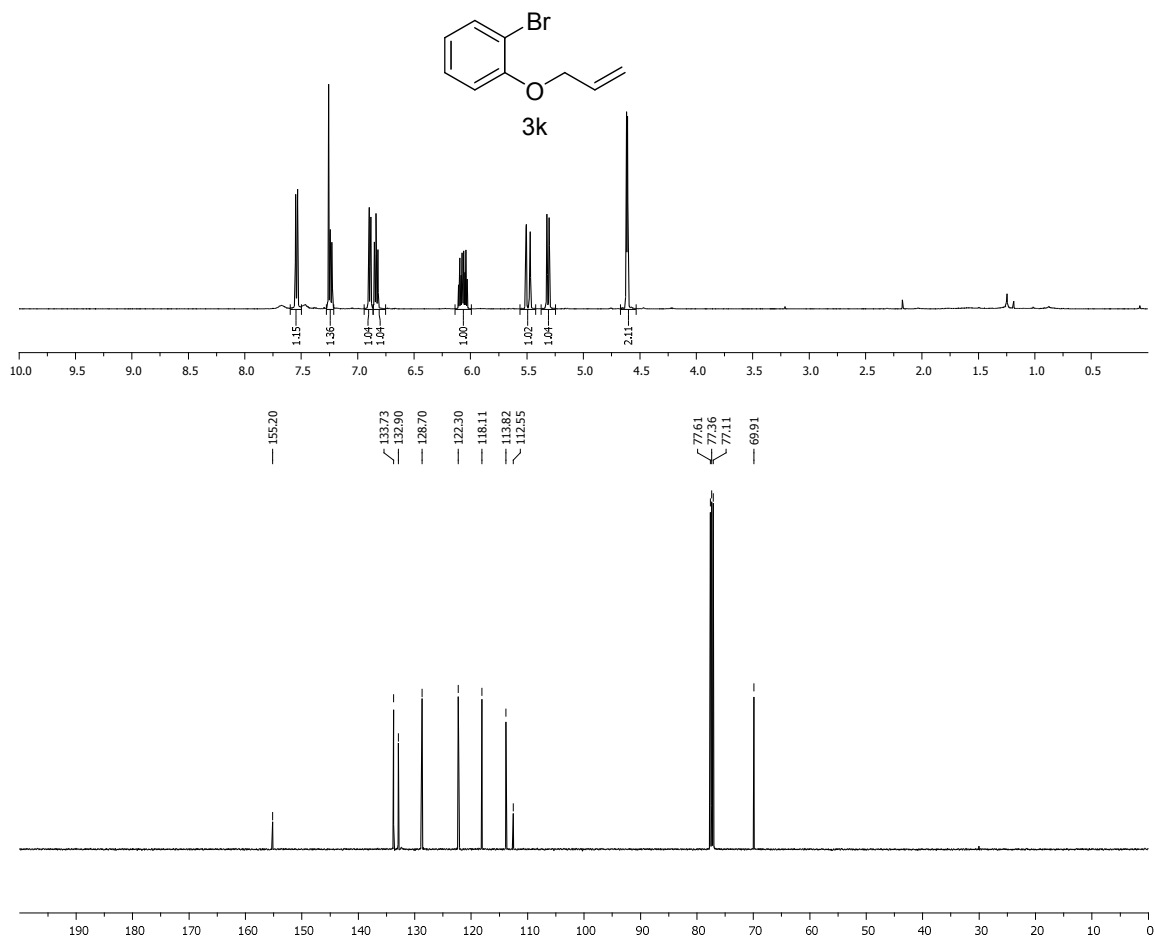


3i: 2-(allyloxy)-4-isopropyl-1-methylbenzene:⁷ Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 7.07 (d, *J* = 7.6, 1H: ArH), 6.75 (d, *J* = 7.6, 1H: ArH), 6.70 (s, 1H: ArH), 6.16 – 5.99 (m, 1H: CH=CH₂), 5.45 (d, *J* = 17.3, 1H: CH=CH₂), 5.28 (d, *J* = 10.6, 1H: CH=CH₂), 4.56 (d, *J* = 5.0, 2H: CH₂-CH=), 2.86 (dt, *J* = 6.9, 13.8, 1H: HC(CH₃)₂), 2.22 (s, 3H: 1-CH₃-Ar), 1.24 (s, 6H: 4-HC(CH₃)₂). ¹³C NMR (126 MHz, CDCl₃) δ 156.9 (Quat., ArC-O), 148.1 (ArC-C(CH₃)₂), 134.1 (CH=CH₂), 130.7 (Ar 6-CH), 124.5 (Quat, Ar 1-C-CH₃), 118.5 (Ar 5-CH), 117.1 (CH=CH₂), 110.1 (Ar 3-CH), 69.0 (O-CH₂-CH=), 34.3 (Ar-HC(CH₃)₂), 24.4 (HC(CH₃)₂), 16.2 (1-CH₃-Ar). v_{max} 2960, 1415, 1093, 1029, 1925, 808 cm⁻¹.

⁷ Petit, P., Bourgeois, P., *J.Chem. Res.*, **2004**, 3, 194 – 195.

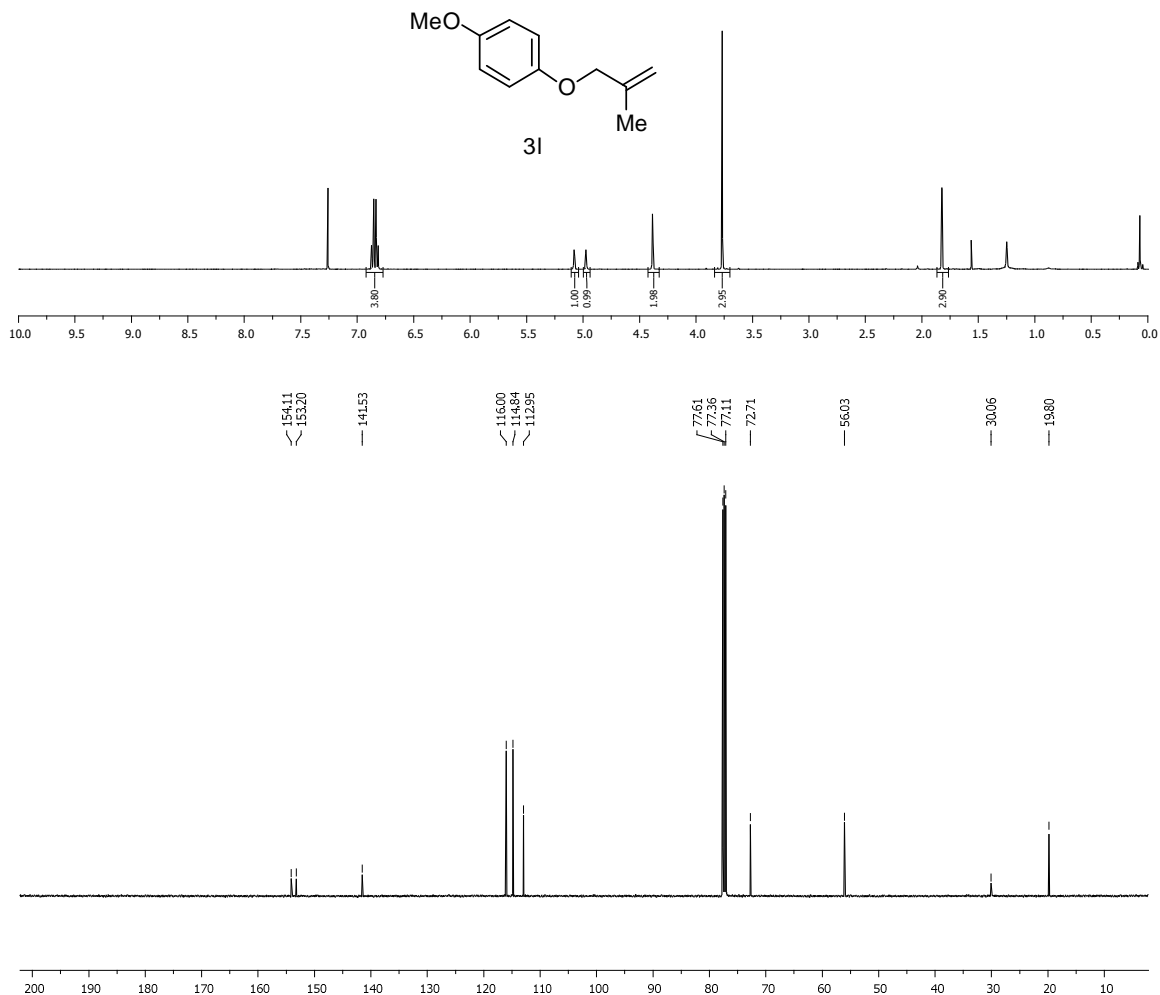


3j: 2-(allyloxy)-1-isopropyl-4-methylbenzene: Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 7.11 (d, *J* = 7.6, 1H: ArH), 6.76 (d, *J* = 7.7, 1H: ArH), 6.67 (s, 1H: ArH), 6.16 – 6.01 (m, 1H: CH=CH₂), 5.44 (d, *J* = 17.3, 1H_E: CH=CH₂), 5.27 (d, *J* = 10.6, 1H_Z: CH=CH₂), 4.54 (d, *J* = 4.9, 2H: CH₂-CH=), 3.33 (dt, *J* = 6.9, 13.8, 1H: HC(CH₃)₂), 2.32 (s, 3H: 1-CH₃-Ar), 1.22 (s, 6H: 4-HC(CH₃)₂). ¹³C NMR (126 MHz, CDCl₃) δ 155.9 (Quat., ArC-O), 136.5 (Quat, Ar 1-C-CH₃), 134.6 (Quat, ArC-C(CH₃)₂), 134.1 (CH=CH₂), 126.2 (ArCH), 121.6 (ArCH), 116.9 (CH=CH₂), 112.9 (ArCH), 69.0 (O-CH₂-CH=), 26.9 (Ar-HC(CH₃)₂), 23.2 (HC(CH₃)₂), 21.7 (1-CH₃-Ar). ν_{max} 2960, 2923, 1415, 1257, 1093, 1029, 808 cm⁻¹; HRMS calcd. for C₁₃H₁₈O (M+Na) 213.1255; found 213.1249.



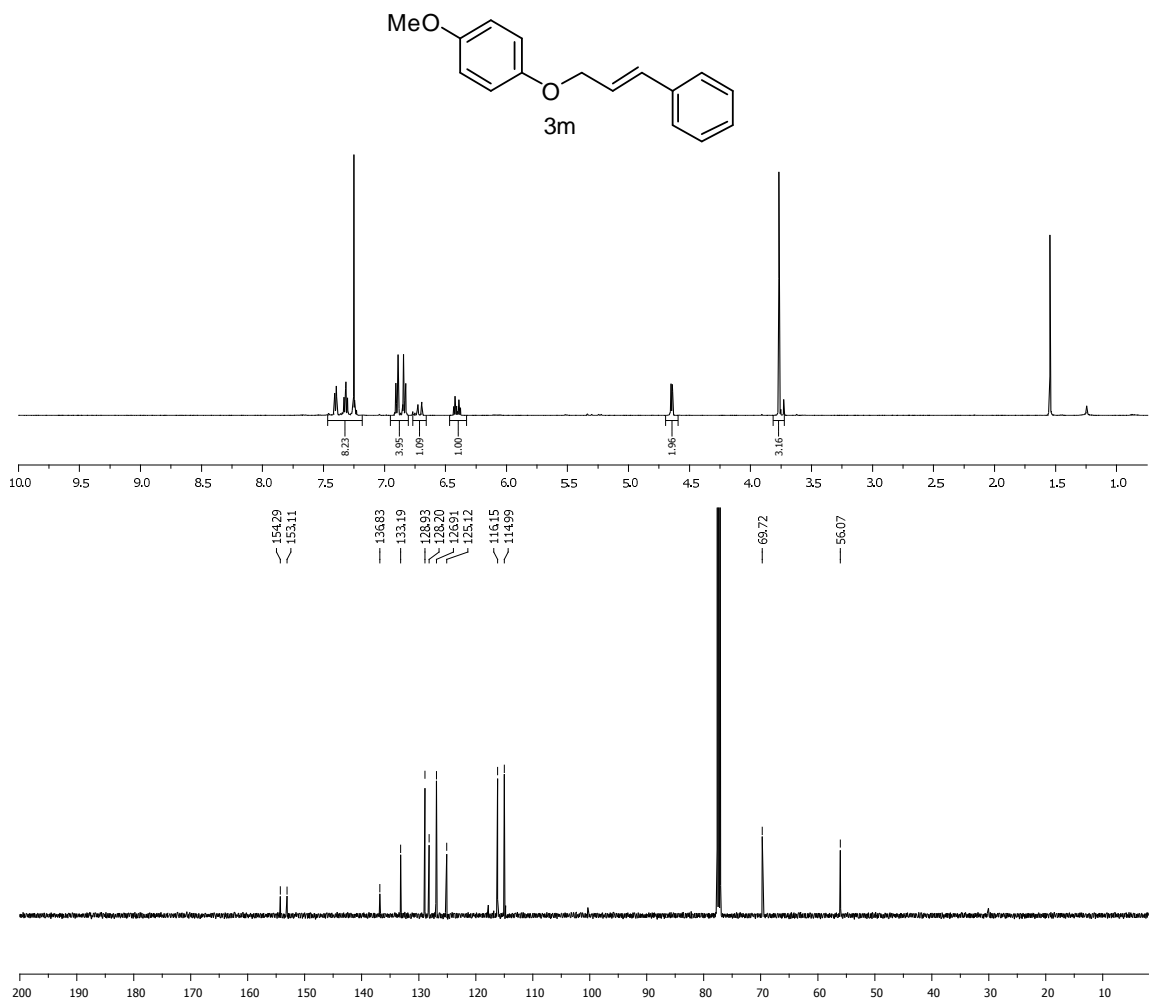
3k: 1-(allyloxy)-2-bromobenzene.⁸ Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 7.54 (d, *J* = 7.9, 1H: ArH), 7.24 (m, 1H: ArH overlapping CHCl₃), 6.90-6.82 (m, 2H: ArH), 6.11 – 6.03 (m, 1H: CH=CH₂), 5.49 (d, *J* = 17.3, 1H_E: CH=CH₂), 5.31 (d, *J* = 10.6, 1H_Z: CH=CH₂), 4.52 (d, *J* = 5.0, 2H: CH₂-CH=). ¹³C NMR (126 MHz, CDCl₃) δ 155.2 (Quat, ArC-O-CH₂), 133.7 (CH=CH₂), 132.7 (ArCH), 128.7 (ArCH), 122.3 (ArCH), 118.1 (CH=CH₂), 113.8 (ArCH), 112.5 (Quat, ArC-Br), 69.9 (O-CH₂-CH=). *v*_{max} 1479, 1292, 1276, 1247, 1051, 997, 929 cm⁻¹.

⁸ Anson, C. E., Malkov, A. V., Roe, C., Sandoe, E. J., Stephenson, G. R., Euro. J. Org. Chem., 2008, 1, 196 – 213.

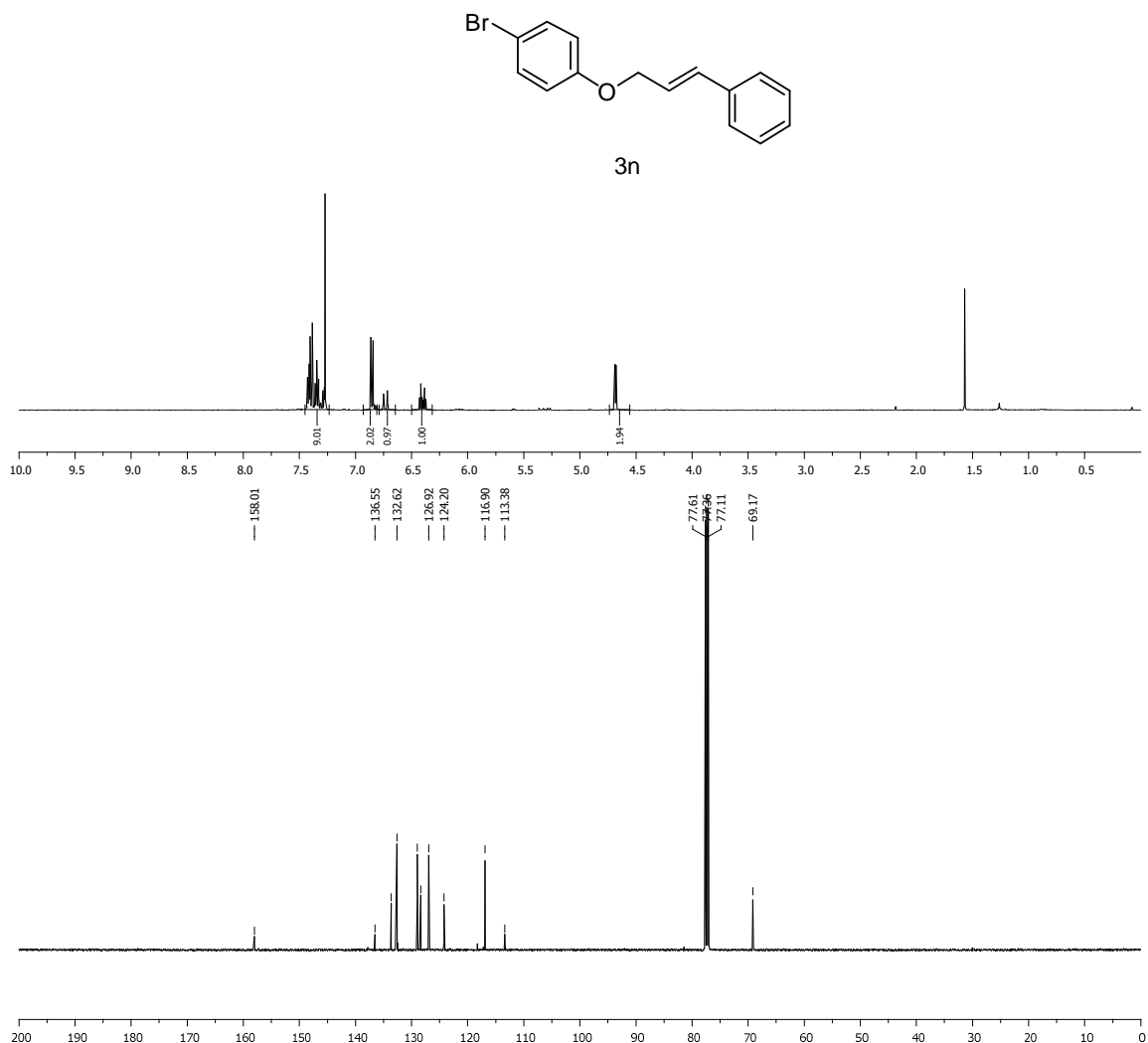


3l: 1-(allyloxy)-4-methoxybenzene:⁹ Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 6.84 (q, *J* = 9.3, 4H:ArH), 5.08 (d, *J* = 0.7, 1H: -C(CH₃)=CH₂), 4.97 (s, 1H: -C(CH₃)=CH₂), 4.38 (s, 2H: CH₂-C(CH₃)), 3.77 (s, 3H: O-CH₃), 1.87 (s, 3H: -C(CH₃)=CH₂). ¹³C NMR (126 MHz, CDCl₃) δ 154.1 (Quat, ArC-OMe), 153.2 (Quat, ArC-O-CH₂), 141.5 (Quat, -C(CH₃)=CH₂), 116.0 & 114.8 (ArCH), 112.9 (-C(CH₃)=CH₂), 72.7 (O-CH₂-C=), 56.0 (CH₃-OAr), 19.8 (-C(CH₃)=CH₂) v_{max} 2929, 1508, 1228, 1039, 823 cm⁻¹.

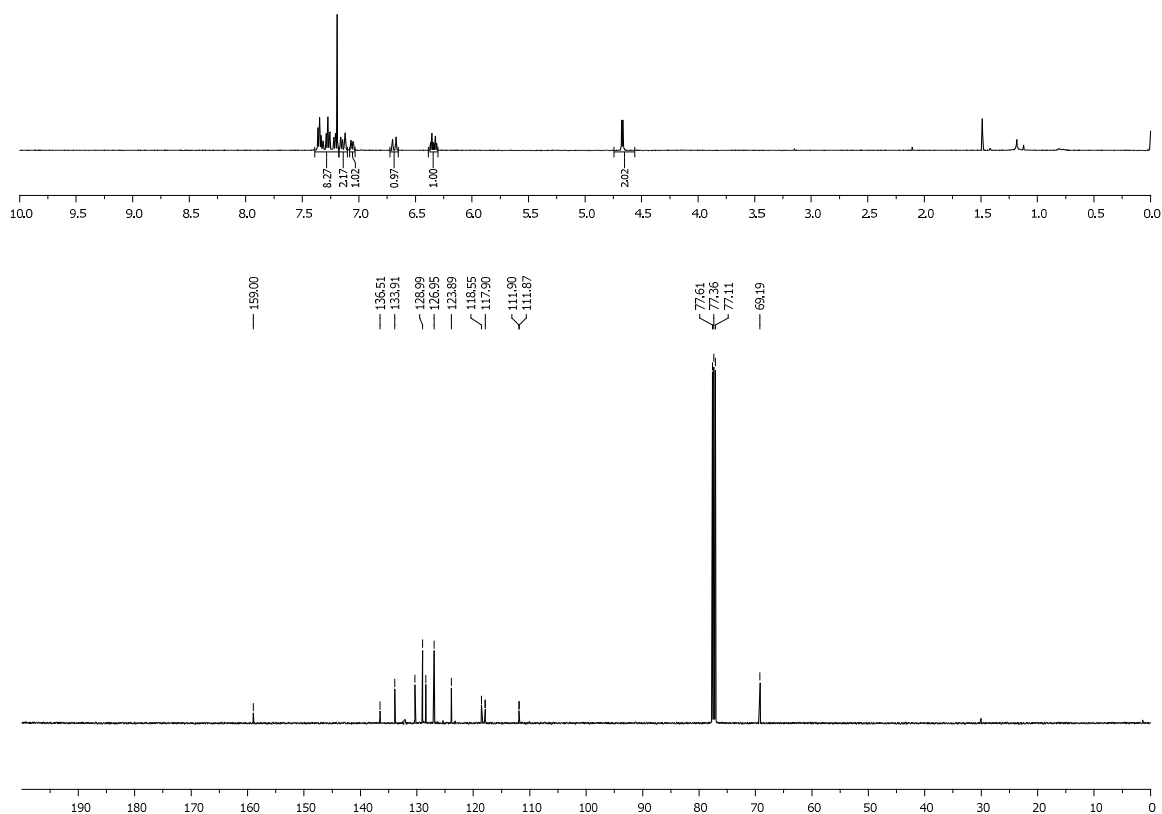
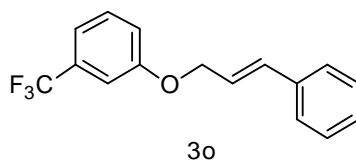
⁹ Wolter, M., Nordmann, G., Job, G. E., Buchwald, S., *Org. Lett.*, **2002**, 4, 973 – 976.



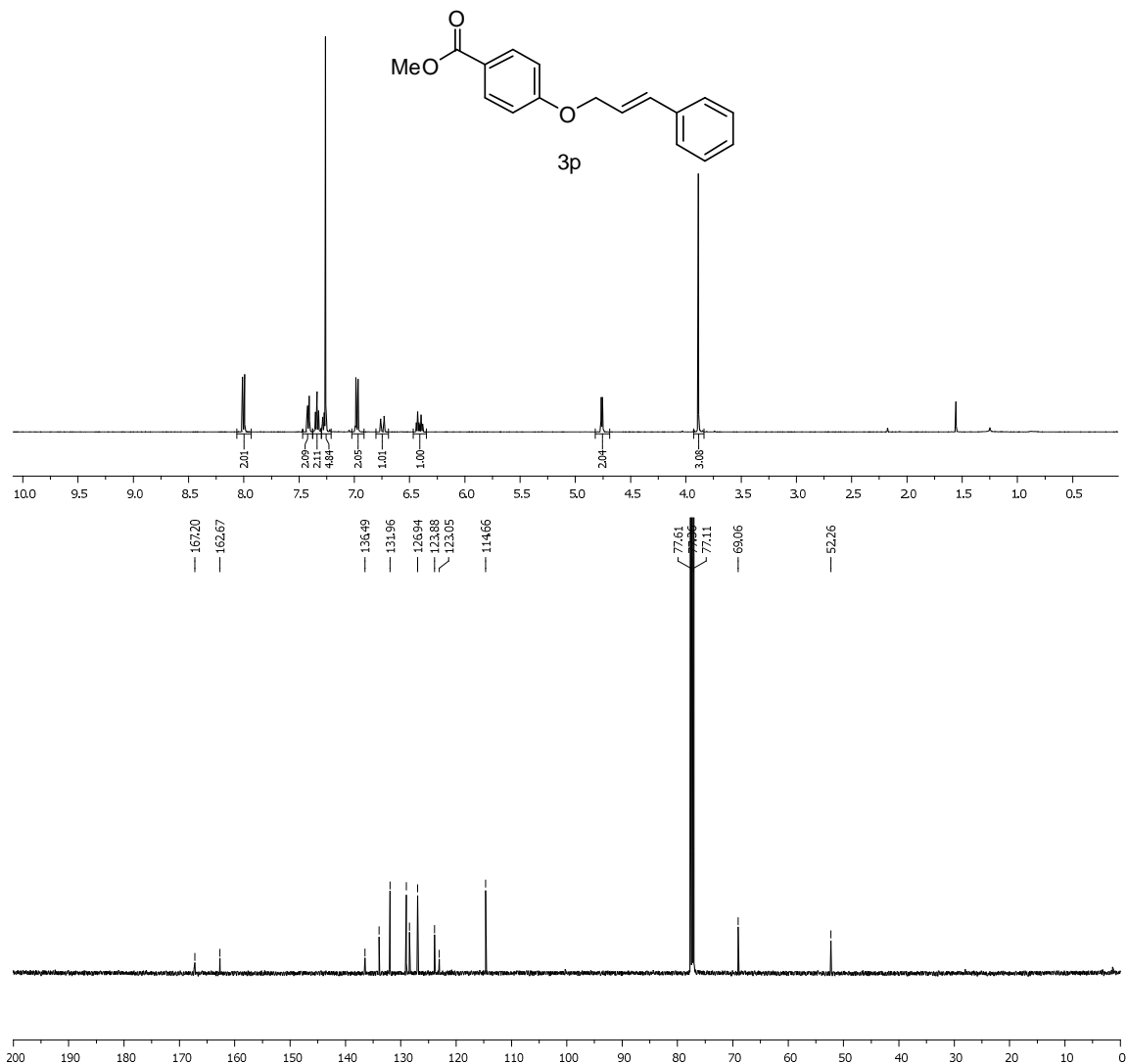
3m: 1-(cinnamyloxy)-4-methoxybenzene: White solid; ¹H NMR (500 MHz, CDCl₃) δ 7.47 – 7.18 (m, 8H: ArH overlapping CHCl₃), 6.87(dd, *J* = 9.2, 31.9, 4H: ArH), 6.72 (d, *J* = 16.0, 1H: CH=CH-CH₂), 6.43–6.38 (m, 1H: CH=CH-CH₂), 4.65 (d, *J* = 5.8, 2H: CH=CH-CH₂), 3.77 (s, 3H: OCH₃). ¹³C NMR (126 MHz, CDCl₃) δ 154.3, (Quat, ArC-OMe), 153.1 (Quat, ArC-O), 136.8 (Quat, ArC-CH=CH), 133.2 (ArCH), 128.9 (ArCH), 128.2 (ArCH), 126.9 (CH=CH-CH₂), 125.1 (CH=CH-CH₂), 116.1 (ArCH), 114.9 (ArCH), 69.7 (O-CH₂-CH=), 56.1 (CH₃O-Ar). v_{max} 2852, 1501, 1401, 1218, 1132, 880 cm⁻¹. HRMS calcd. for C₁₆H₁₆O₂ (M+H) 241.1229; found 241.1239.



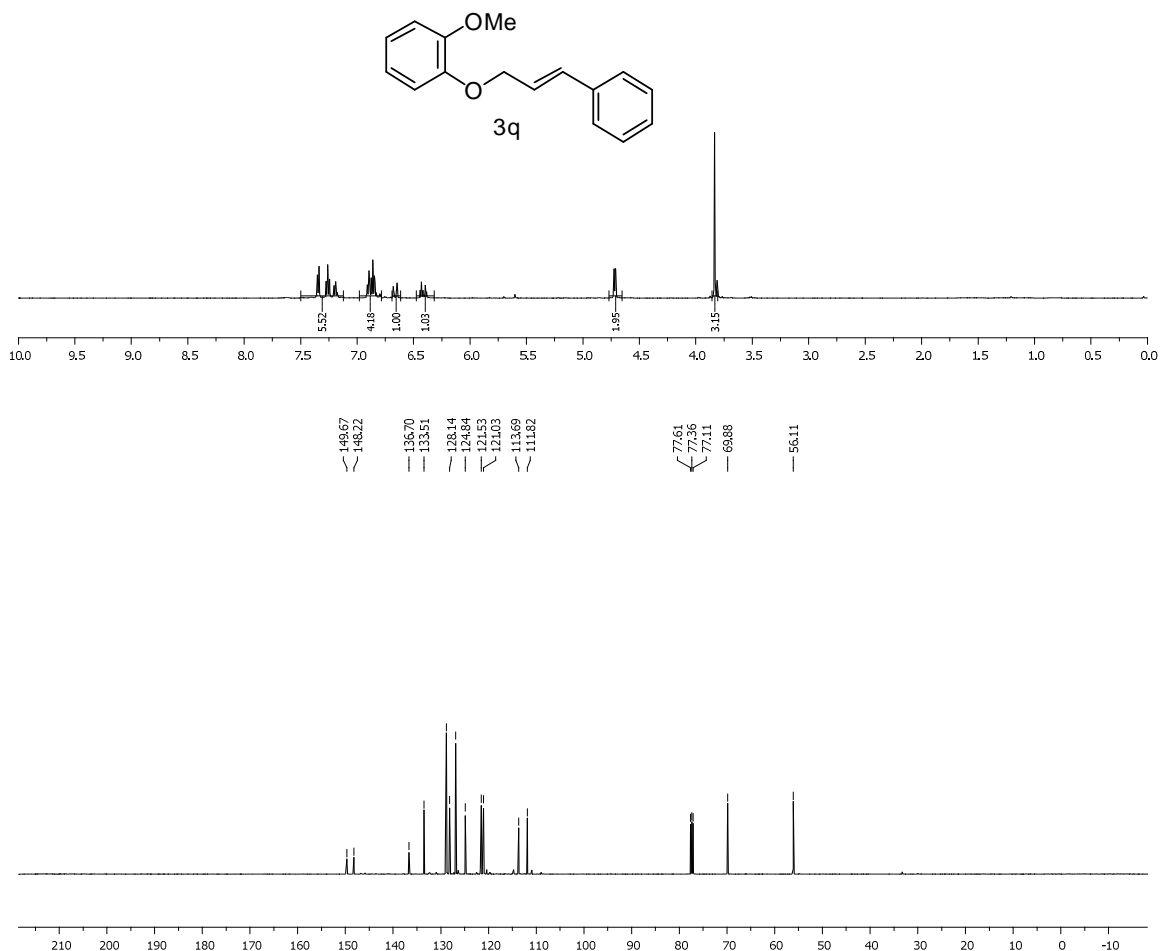
1-bromo-4-(cinnamyloxy)benzene: White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.45 – 7.24 (m, 7H: ArH overlapping CHCl_3), 6.85(d, $J = 9.1$, 2H: ArH), 6.73 (d, $J = 16.0$, 1H: $\text{CH}=\text{CH}-\text{CH}_2$), 6.43-6.37 (m, 1H: $\text{CH}=\text{CH}-\text{CH}_2$), 4.68 (d, $J = 5.8$, 2H: $\text{CH}=\text{CH}-\text{CH}_2$). ^{13}C NMR (126 MHz, CDCl_3) δ 158.0 (Quat, ArC-O), 136.5 (Quat, ArC-CH=CH), 133.5 (Ar 2,6-CH), 128.9 (ArCH), 128.3 (ArCH), 126.9 ($\text{CH}=\text{CH}-\text{CH}_2$), 124.2 ($\text{CH}=\text{CH}-\text{CH}_2$), 116.9 (Ar 3,5-CH), 113.1 (Quat, ArC-Br), 69.7 (O-CH₂-CH=). ν_{max} 2148, 1949, 1487, 1240, 692 cm^{-1} . HRMS calcd. for $\text{C}_{15}\text{H}_{13}\text{BrO}$ (M+Na) 311.0047; found 311.0066.



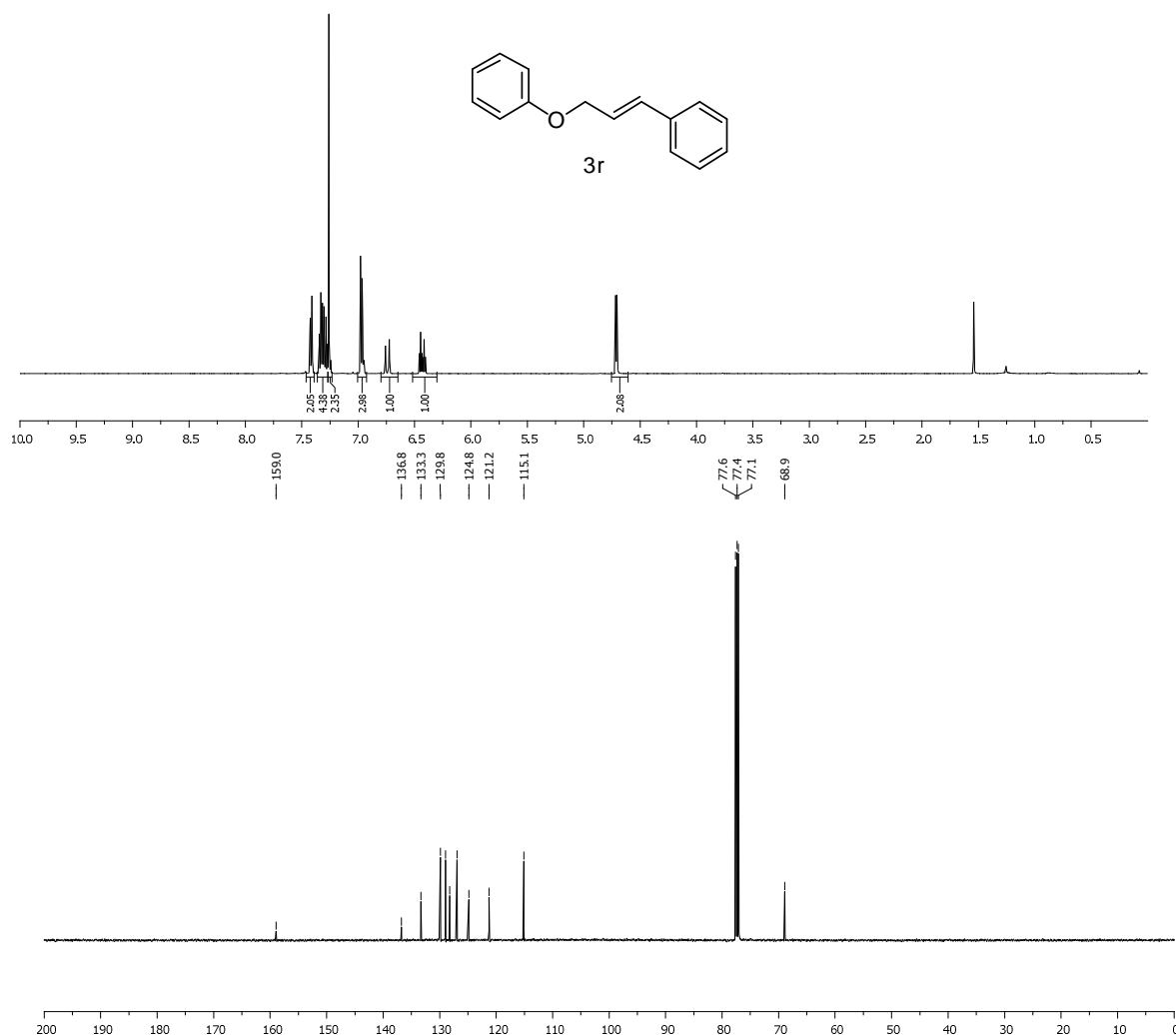
30: 1-(cinnamyloxy)-3-(trifluoromethyl) benzene: White solid; ^1H NMR (500 MHz, CDCl_3) δ 7.39 – 7.05 (m, 12H: ArH overlapping CHCl_3), 6.69(d, $J = 16.0$, 1H: $\text{CH}=\text{CH}-\text{CH}_2$), 6.37-6.31 (m, 1H: $\text{CH}=\text{CH}-\text{CH}_2$), 4.67 (d, $J = 5.8$, 2H: $\text{CH}=\text{CH}-\text{CH}_2$). ^{13}C NMR (126 MHz, CDCl_3) δ 159.0 (Quat, $\text{ArC}-\text{O}$), 136.5 (Quat, $\text{ArC}-\text{CH}=\text{CH}$), 133.9 (ArC), 130.3 (ArC), 128.9 (ArC), 126.4 ($\text{CH}=\text{CH}-\text{CH}_2$), 126.9 ($\text{CH}=\text{CH}-\text{CH}_2$), 123.9 (ArC), 118.5 (ArC), 117.9(ArC), 69.1 ($\text{O}-\text{CH}_2-\text{CH}=\text{}$). Can't detect CF_3 and CF_3-CAr quaternary carbons. ν_{max} 2923, 1591, 1326, 1126, 1020, 792 cm^{-1} ; HRMS calcd. for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{O}$ ($\text{M}+\text{Na}$) 301.0816; found 301.0818.



3p: Methyl 4-(cinnamyloxy)benzoate: White solid; ¹H NMR (500 MHz, CDCl₃) δ 8.00 (d, *J* = 9.0, 2H: ArH), 7.47 – 7.21 (m, 9H: ArH overlapping CHCl₃), 6.98(d, *J* = 9.0, 2H: 2,6-ArH), 6.75 (d, *J* = 16.0, 1H: CH=CH-CH₂), 6.44-6.38 (m, 1H:CH=CH-CH₂), 4.76 (d, *J* = 5.8, 2H: CH=CH-CH₂), 3.89 (s, 3H: CH₃OCO), ¹³C NMR (126 MHz, CDCl₃) δ 167.2 (Quat, CH₃OCO), 162.6 (Quat, ArC-O), 136.5 (Quat, ArC-CH=CH), 133.9 (ArCH), 131.9 (ArCH), 128.9 (ArCH), 128.4 (CH=CH-CH₂), 126.9 (CH=CH-CH₂), 123.8 (ArCH), 123.0 (Quat, ArC-COOCH₃), 114.6 (ArCH), 113.1 (Quat, ArC-Br), 69.0 (O-CH₂-CH=), 52.26 (CH₃OCO). *v*_{max} 2862, 1456, 1172, 1110, 499 cm⁻¹; HRMS calcd. for C₁₇H₁₆O₃ (M+H) 269.1178; found 269.1190.



3q: 1-(cinnamyloxy)-2-methoxybenzene: White solid; ¹H NMR (500 MHz, CDCl₃) δ 7.50 – 7.12 (m, 6H: ArH overlapping CHCl₃), 6.98 – 6.78 (m, 4H: ArH), 6.66 (d, *J* = 16.0, 1H: CH=CH-CH₂), 6.44-6.39 (m, 1H: CH=CH-CH₂), 4.72 (d, *J* = 5.9, 2H: CH=CH-CH₂), 3.83 (s, 3H: OCH₃). ¹³C NMR (126 MHz, CDCl₃) δ 149.6, (Quat, ArC-OMe), 148.2 (Quat, ArC-O), 136.7 (Quat, ArC-CH=CH), 133.5 (ArCH), 128.8 (ArCH), 128.1 (ArCH), 126.8 (CH=CH-CH₂), 124.8 (CH=CH-CH₂), 121.5 (ArCH), 121.0 (ArCH), 113.7 (ArCH), 111.82 (ArCH), 69.8 (O-CH₂-CH=), 56.1 (CH₃O-Ar). *v*_{max} 1479, 1332, 1284, 1180, 696 cm⁻¹; HRMS calcd. for C₁₆H₁₆O₂ (M+H) 241.1229; found 241.1239.



3r: (3-Phenylprop-2-enyl)oxy-benzene:¹⁰ White solid; ¹H NMR (500 MHz,

CDCl₃) δ 7.42 (d, *J* = 7.3, 2H:ArH), 7.36 – 7.23 (m, 5H:ArH), 7.00 – 6.92 (m,

3H:ArH), 6.74 (d, *J* = 16.0, 1H: CH=CH-CH₂), 6.46-6.40 (m, 1H:CH=CH-CH₂),

4.71 (d, *J* = 5.8, 2H: CH=CH-CH₂). ¹³C NMR (126 MHz, CDCl₃) δ 158.9 (Quat,

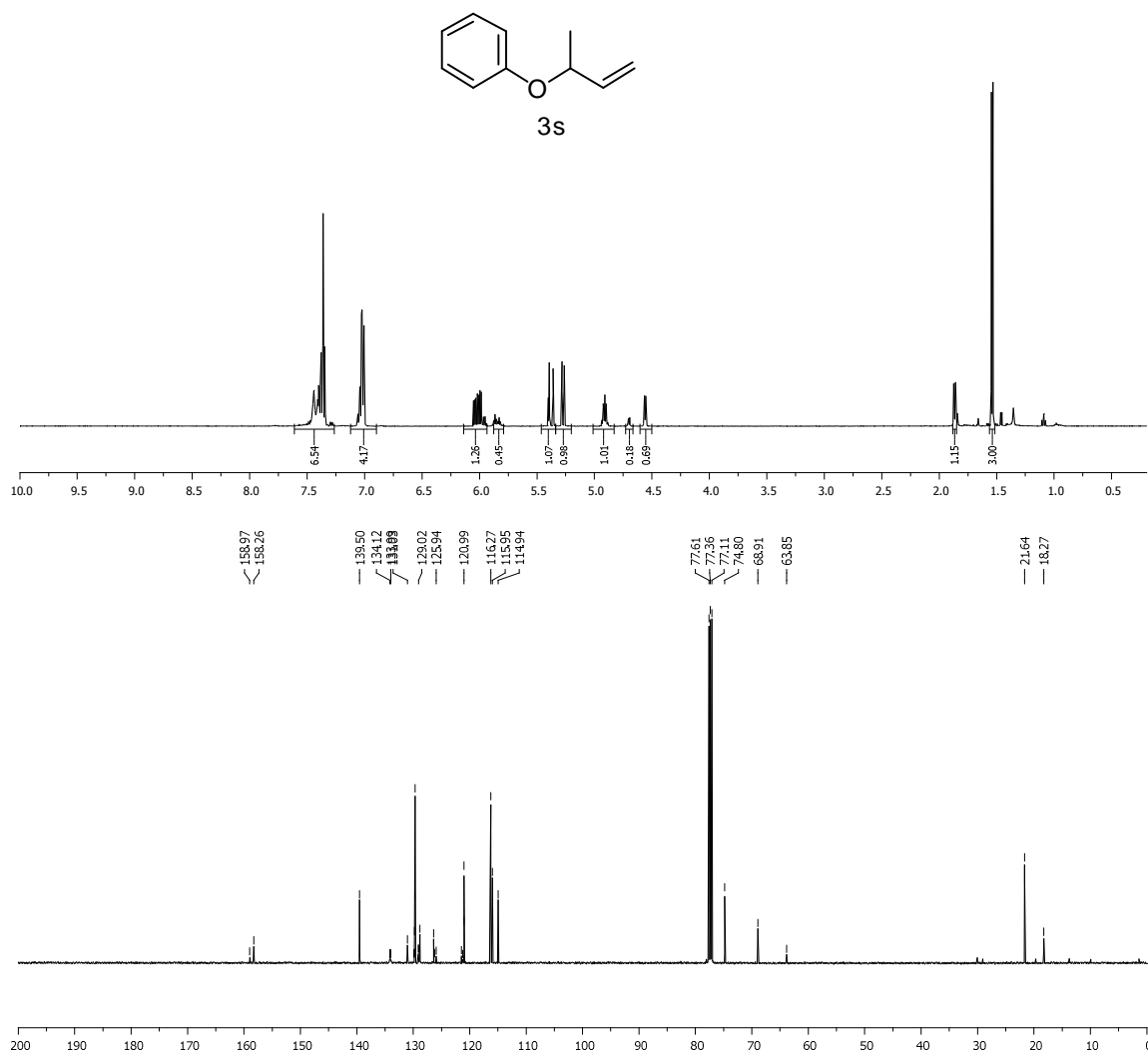
ArC-O), 136.7 (Quat, ArC-CH=CH), 133.3 (Ar 3,5-C), 129.8 (Ar4-C), 128.9 (Ar

2-C), 128.2 (Ar 6-C), 126.9 (CH=CH-CH₂), 124.8 (CH=CH-CH₂), 121.2 (Ar 4-C),

115.1 (Ar 2,6-C), 68.9 (O-CH₂-CH=). *v*_{max} 1598, 1242, 1012, 962, 740, 692 cm⁻¹

1.

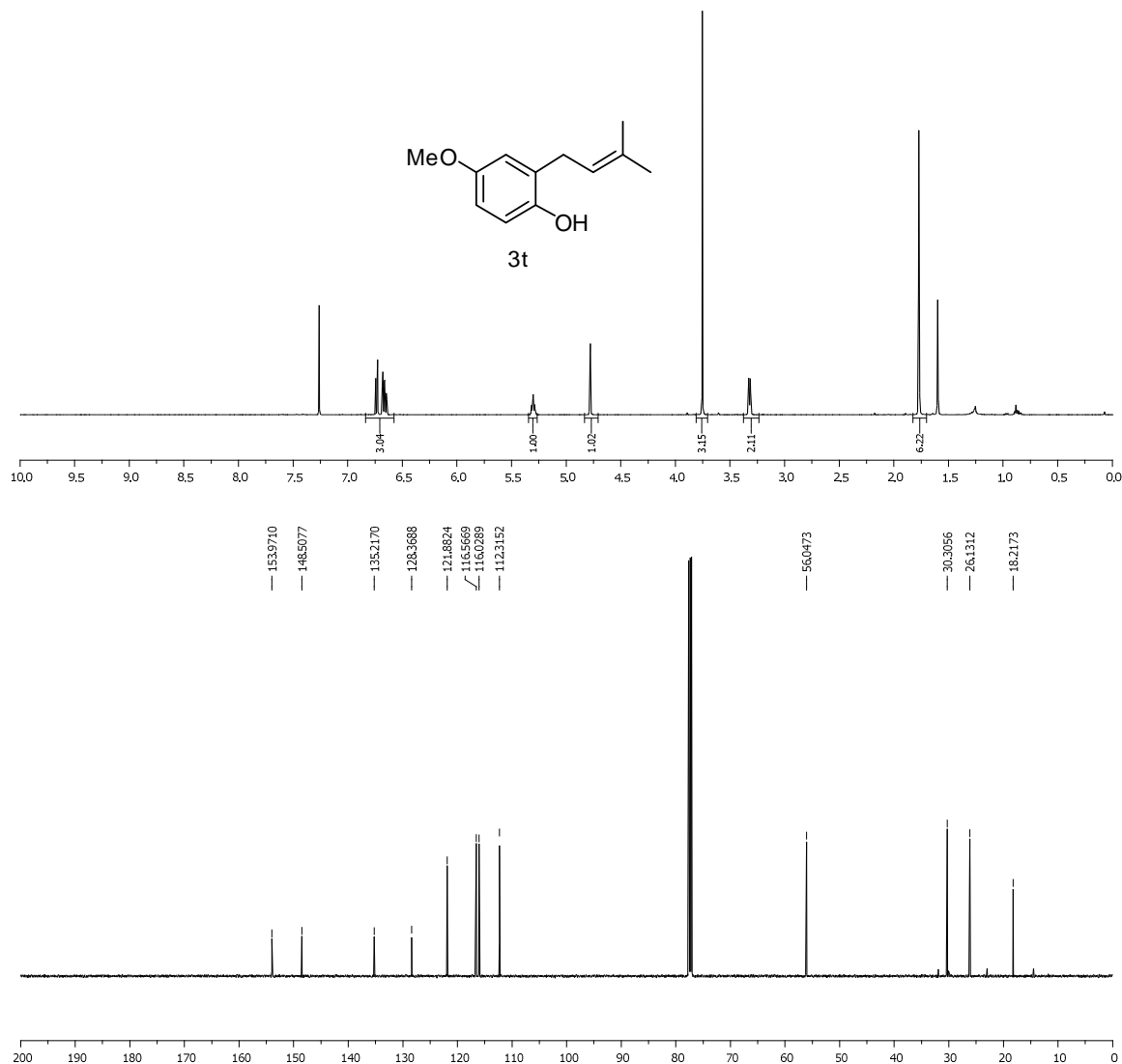
¹⁰ Satoh T., Ikeda M., Miura M., Nomura M., *J. Org. Chem.*, **1997**, 62, 4877 – 4879.



3s: (but-3-en-2-yloxy) benzene:¹¹ Colorless oil; 25% linear product was obtained. ¹H NMR (500 MHz, CDCl₃) δ 7.51 – 6.8 (m, 11H: ArH of both regioisomers, overlapping with CHCl₃), 6.04 – 5.83 (m, 1H:CH=CH₂:branched overlapping with -CH=CH-CH₃ of minor linear isomer), 5.78 – 5.69 (m, CH=CH₂:linear), 5.28 (d, *J* = 17.3, 1H_E:CH=CH₂), 5.17 (d, *J* = 10.6, 1H_Z:CH=CH₂), 4.91 – 4.73 (m, 1H:ArO-CH(CH₃)CH=), 4.63 – 4.40 (d, ArO-CH₂:linear), 1.77 (d, *J* = 6.4, -CH=CH-CH₃:linear), 1.44 (d, *J* = 6.4, 3H: ArO-CH₃:linear).

¹¹ Satoh T., Ikeda M., Miura M., Nomura M., *J. Org. Chem.*, **1997**, 62, 4877 – 4879.

CH(CH₃)-CH=CH₂). ¹³C NMR (126 MHz, CDCl₃) δ 158.9 (Quat, ArC-O-CH₂ (linear)), 158.2 (Quat, ArC-O-CH(CH₃) (branched)), 139.5 (CH=CH₂), 134.1 ((ArCH), 134.0 (ArCH), 133.9 (ArCH), 133.0 (ArCH), 131.0 (ArCH), 129.9 (ArCH), 128.8 (CH₂CH=CH-CH₃:linear), 126.3 (CH₂CH=CH-CH₃:linear), 121.4 (ArCH), 116.2 (ArCH), 115.9 (CH=CH₂), 114.9 (ArCH), 74.8 (ArO-(CH₃)CH-CH=CH₂), 68.9 (ArO-CH₂-CH=CH-:linear), 21.6 (ArO-(CH₃)CH-CH=CH₂), 18.2 (-CH₂CH=CH-CH₃:linear). v_{max} 2950, 1589, 1471, 1170, 1039, 993 cm⁻¹.



3t: 4-methoxy-2-(3-methylbut-2-enyl): Colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 6.84 – 6.58 (m, 3H: ArH), 5.34 – 5.27 (m, 1H: CH=CH₂), 4.78 (s, 1H: Ar-OH), 3.75 (s, 3H: Ar-OCH₃), 3.32 (d, *J* = 7.2, 2H: Ar-CH₂-CH=C(CH₃)₂), 1.83 – 1.70 (m, 6H: Ar-CH₂-CH=C(CH₃)₂). ¹³C NMR (126 MHz, CDCl₃) δ 153.9 (Quat., ArC-OMe), 148.5 (Quat., ArC-OH), 135.2 (Quat., Ar-CH₂-CH=C(CH₃)₂), 128.3 (Quat., ArC-CH₂-CH=), 121.8 (Ar-CH₂-CH=C(CH₃)₂), 116.5 (Ar-CH), 116.0 (Ar-CH), 112.3 (Ar-CH), 56.0 (ArC-OCH₃), 30.3 (Ar-CH₂-CH=C(CH₃)₂), 26.1 (Ar-CH₂-CH=C(CH₃)₂), 18.2 (Ar-CH₂-CH=C(CH₃)₂). v_{max} 3423, 3404, 2960,

2923, 2854, 2835, 1504, 1433, 1276, 1201, 1110, 1041, 923, 802, 786 cm^{-1} ;

HRMS calcd. for $\text{C}_{13}\text{H}_{18}\text{OH}$ (M+Na) 215.1048 found 215.1037.

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Part 3: Palladium-catalyzed decarboxylative sp^2 - sp^3 coupling of coumarins

3.1 Approach

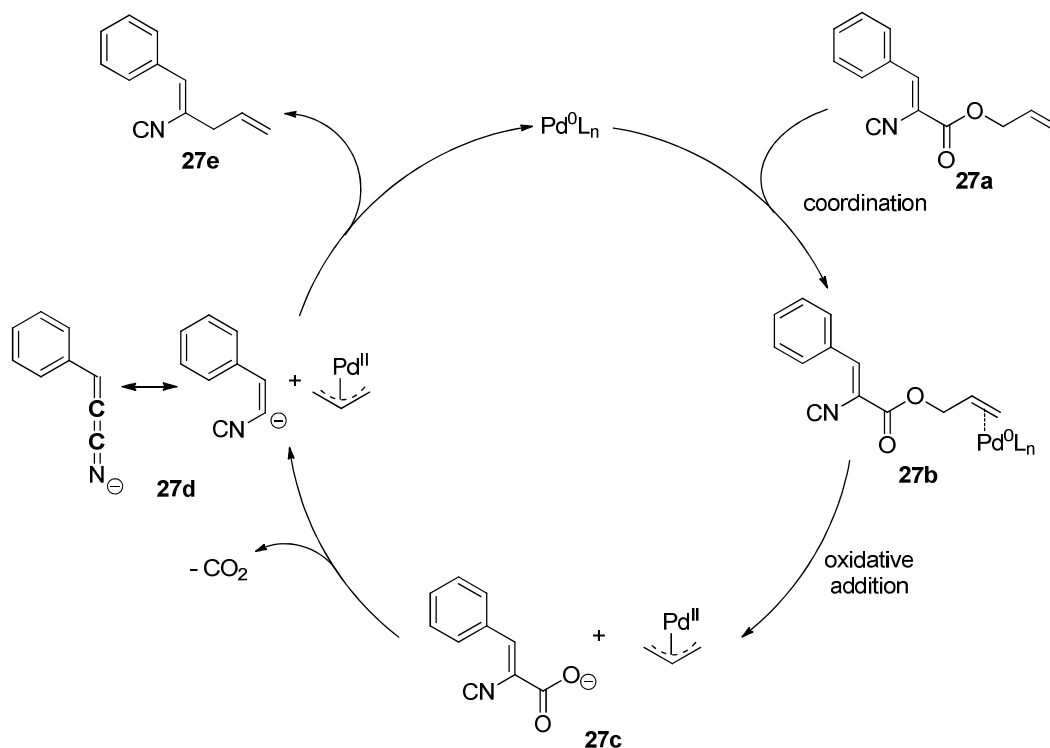
After a thorough search in literature, we discovered, that decarboxylative sp^2 - sp^3 couplings were relatively rare, and required typically harsh temperature conditions and heavy catalyst and co-catalyst loadings.¹⁻⁵ In order to circumvent these issues, we embarked upon the discovery of a mild and efficient way to achieve a decarboxylative sp^2 - sp^3 coupling.

We started out with a strategy where we employed an electron withdrawing group (EWG) on a vinyl allyl ester (Scheme 27). We reasoned that the EWG on the vinyl carbon should help stabilize the incipient negative charge at the vinyl carbon as decarboxylation occurs. Thus we began working on esters of cyano acrylates (**27a**) as a starting point. Our rationale was that after the formation of the π -allylpalladium species, the resulting cyanoacrylate acetate (**27c**) would decarboxylate to generate a cyano-stabilized vinyl anion (**27d**). Subsequent coupling of the anion (**27d**) with π -allyl palladium species would lead to the formation of the coupling product (**27e**) and return the Pd(0) catalyst. The crux of the whole strategy was embedded in the fact that the generation of a vinyl anion (**27d**) would be an unfavorable process and require stabilization from an electron withdrawing group like nitrile.

Although this scheme seems feasible on paper, when put in practice, only about 2-3% of the coupling product **27e** was isolated. Most of the starting material decarboxylated to give the cyanoacrylate and some polymerized products. Similar results were obtained with other electron withdrawing groups too. However, it is

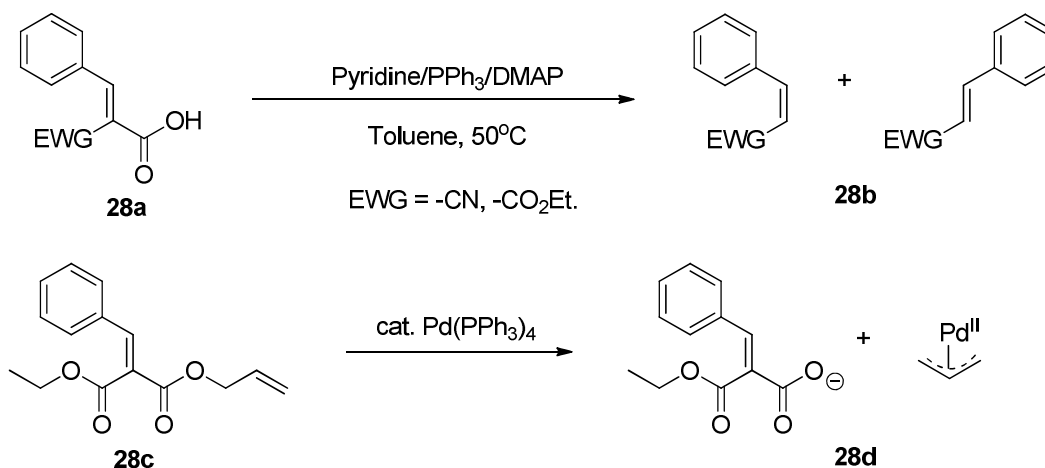
important to mention here, that Saegusa⁶ has shown the decarboxylation of allyl 2-cyano-2-cyclohexylideneacetate in the presence of $\text{Pd}(\text{PPh}_3)_4$.

Scheme 27: Strategy for sp^2 - sp^3 coupling



Interestingly, when an ester is employed as an EWG (**28c**), quantitative π -allylpalladium formation (**28d**) was observed by ^1H NMR spectroscopy. Digging deeper into literature, we found that Corey^{7,8} has shown in the early 50's, that 2-cyanoacrylic acids (**28a**) readily decarboxylate in presence of nucleophiles like DMAP and pyridine. We were able to replicate the same decarboxylation with triphenylphosphine as nucleophile and nitrile or esters as the EWG.

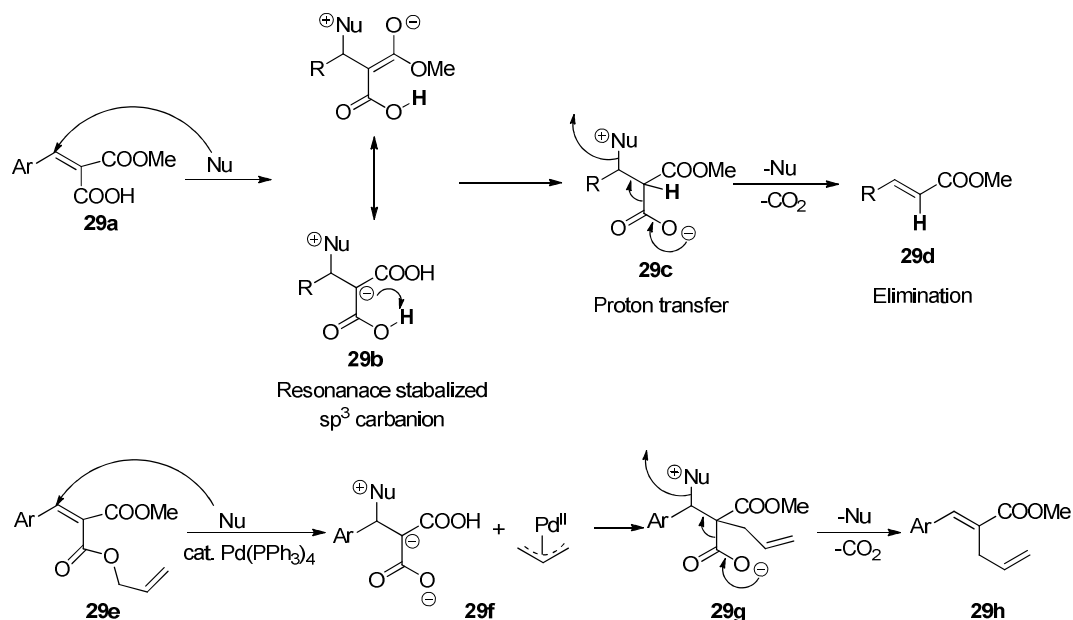
Scheme 28: Decarboxylation of aryl acrylates



3.2 Proof of concept

Corey has investigated the mechanism^{7,8} for this decarboxylation very extensively and more recently, Bernhardt Breit^{9,10} has also used this decarboxylation trick in a decarboxylative hydroformylation. They propose the attack of a nucleophile on the double bond in order to generate a sp^3 anion **29b**. This resonance stabilized sp^3 anion can undergo a proton transfer and pick up a proton from the acid to generate the carboxylate **29c**. Subsequently decarboxylation can occur to regenerate the double bond and quench the charge on the nucleophile to give the product **29d**.

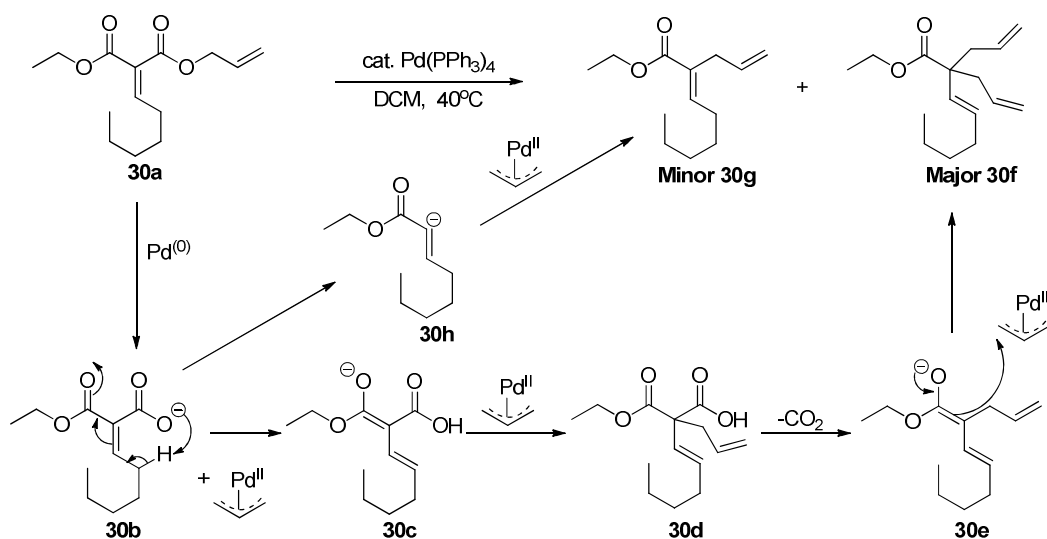
Scheme 29: Mechanism



Looking at the above data, we decided to employ this strategy for our coupling process. We synthesized allyl esters of methylidene malonates (**29e**) replacing the carboxylic acid proton with an allyl group. Much to our disappointment, we did not achieve any C–C bond formation (**29h**) in presence of $\text{Pd}(\text{PPh}_3)_4$. We assumed that the phenyl group of **28c** was making the benzylic position stable and not as electrophilic as we would like it to be. Thus we removed the aromatic ring and replaced it with an alkyl chain. Treatment of substrate **30a** with $\text{Pd}(\text{PPh}_3)_4$ gave us an unexpected result, providing diallylated product **30f** as the major product in 43% yield. ~5% monoallylated sp^2 - sp^3 coupled product **30g** was also observed. We can explain the formation of diallylated product as explained in scheme 30. In presence of $\text{Pd}(\text{PPh}_3)_4$, **30a** can form the π -allylpalladium and the carboxylate anion **30b**. At this point of time, a

simple proton transfer to the carboxylate from the acidic γ -protons of the methyldiene malonate leads to the enolate **30c**. This enolate can attack the electrophilic π -allylpalladium to give **30d**. Decarboxylation of **30d** will again give us an enolate **30e**, which can react with another π -allylpalladium to give the major diallylated product **30f**. However, if **30b** decarboxylates to form a vinyl anion **30h** and subsequently attacks a π -allylpalladium, we get the minor product **30g**.

Scheme 30: Diallylation

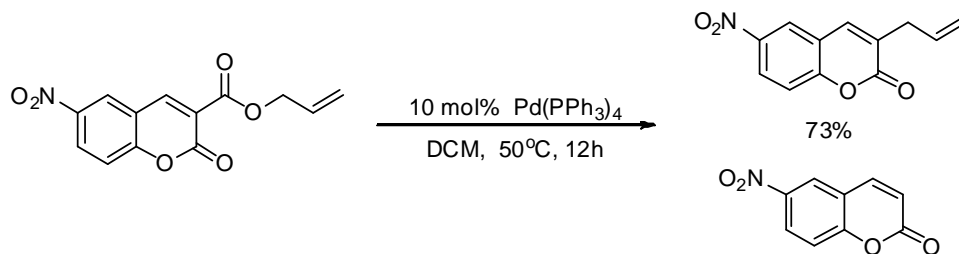


After the above observation, we realized that presence of acidic protons alpha to the double bond, is facilitating this diallylation process. Thus we chose to investigate related carboxycoumarin substrates which are analogs of alkylidene malonates that lack acidic γ -protons. Herein, we discuss the results.

3.3 Initial Experiments

To begin, Dr. Ranjan Jana and I synthesized allyl 4-nitro-2-oxo-2H-chromene-3-carboxylate and treated it with $\text{Pd}(\text{PPh}_3)_4$ in CH_2Cl_2 (Scheme 31). It was gratifying to find the reaction went to 100% conversion, allowing 6-nitro 3-allylcoumarin to be isolated in 73% yield. In addition to the product, approximately 10% yield of 6-nitrocoumarin is also formed, which results from protonation of a putative coumarin anion equivalent.¹¹ We were aware of the fact that decarboxylation of 3-carboxycoumarins can be effected by heating with strong acid or base, decarboxylative metalation under neutral conditions is difficult. For example, copper-catalyzed decarboxylation of a related 2-carboxycoumarin takes place at 248 °C in refluxing quinoline.¹¹⁻¹³ With that in mind, it is particularly noteworthy that the decarboxylative coupling took place at just 50 °C. Moreover, the allylation took place without the need for preformed organometallics that are typically required for the allylation of sp^2 carbons¹⁴⁻¹⁹ and it is more efficient than typical syntheses of 3-allylcoumarins.^{20,21}

Scheme 31: Nitro Coumarin pilot

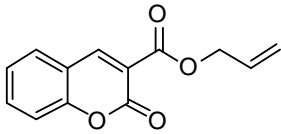
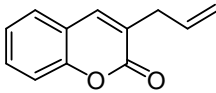
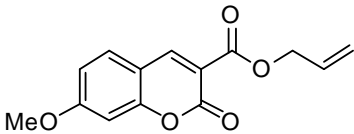
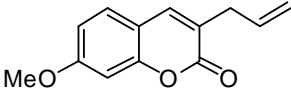
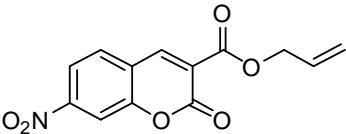
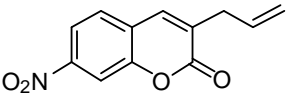
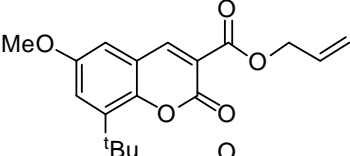
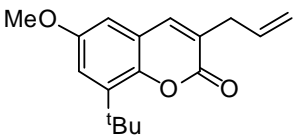
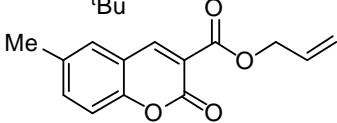
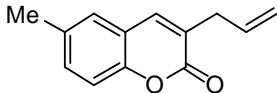
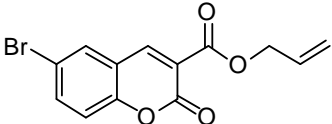
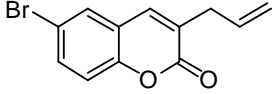
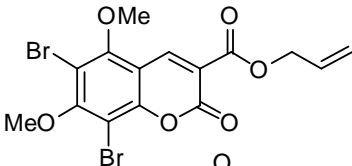
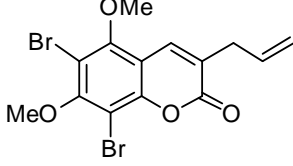
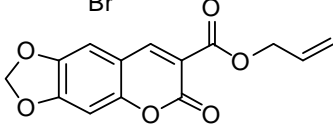
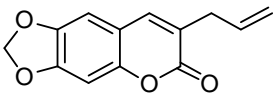
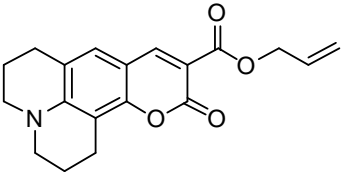
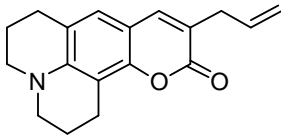
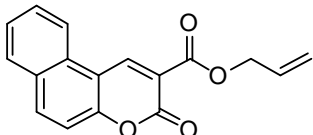
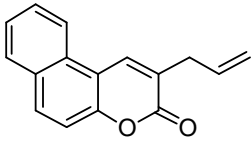


3.4 Scope

Next, a range of coumarins were subjected to our standard conditions for the coupling. As can be seen in Table 4, the yields of the coupling are generally

good. The reaction is compatible with electron-donating and electron-withdrawing functional groups. This fact argues against simple electrophilic allylation of the coumarin.^{22, 23} While coumarins with oxygen donors are excellent substrates, an amine-containing substrate (Table 4, entry 9) provides a relatively low yield of product. Importantly, aryl bromides are tolerated, allowing tandem reactions involving decarboxylative coupling and standard cross-coupling chemistry.

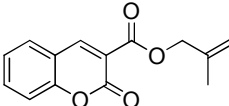
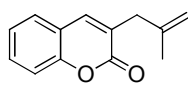
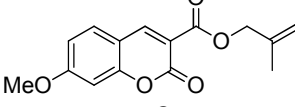
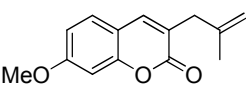
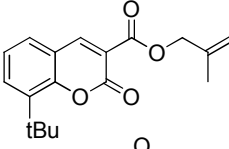
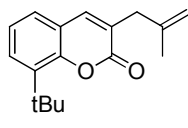
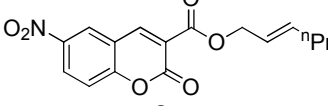
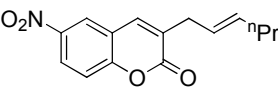
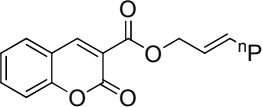
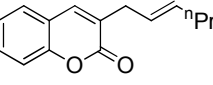
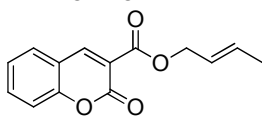
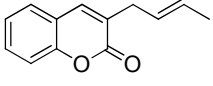
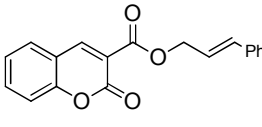
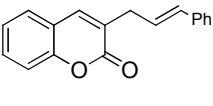
Table 4: *Decarboxylative coupling of Coumarins*

entry	substrate	product	yield (%) ^a
1			67
2			62
3			72
4			62
5			77
6			70
7 ^b			63
8			67
9			37
10			57

^a Isolated yield using 10 mol% Pd(PPh₃)₄, 50°C, 12 - 15h. ^b At room temperature

Next we turned our attention to the investigation of the coupling of substituted allyl electrophiles with coumarins (Table 5). The coupling of 2-methallyl alcohol derivatives proceeds smoothly and provides products in somewhat higher yields than those without methallyl substituents (Table 5, entries 1-3). Importantly, the chemistry is also compatible with 3-alkyl-substituted allyl groups (Table 5, entries 4-6). This is particularly noteworthy because the coupling is the formal allylation of a very basic vinyl anion. Typically, such strong bases simply induce elimination of the π -allyl palladium intermediates.^{24, 25}

Table 5: Decarboxylative coupling of substituted allylic esters.

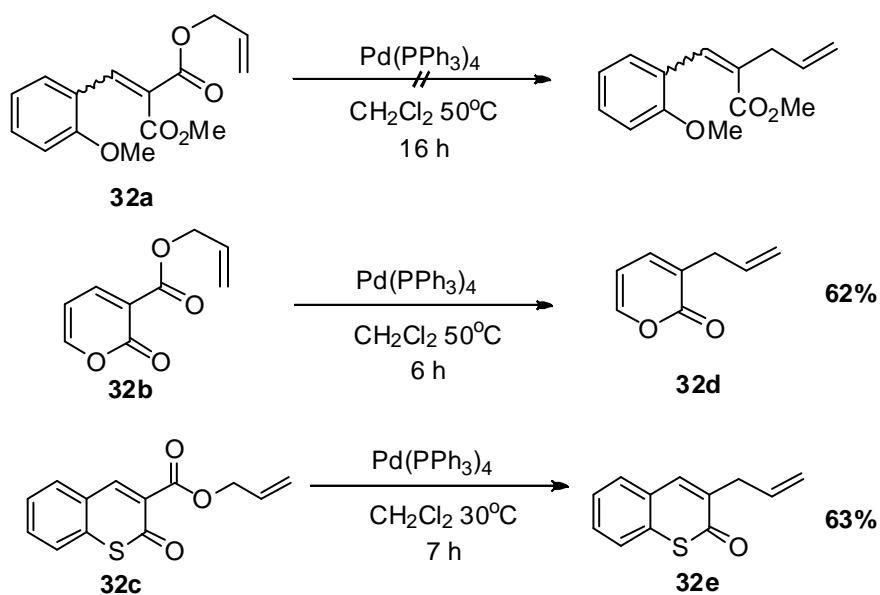
entry	Substrate	Time (h)	Product	Yield (%)
1		12		82
2		10		87
3		10		78
4		12		53
5		12		66
6		15		42 ^a
7		6		81

^a Isolated as a 94:6 mixture of linear:branched regioisomers.

3.5 Mechanistic investigations and Extensions

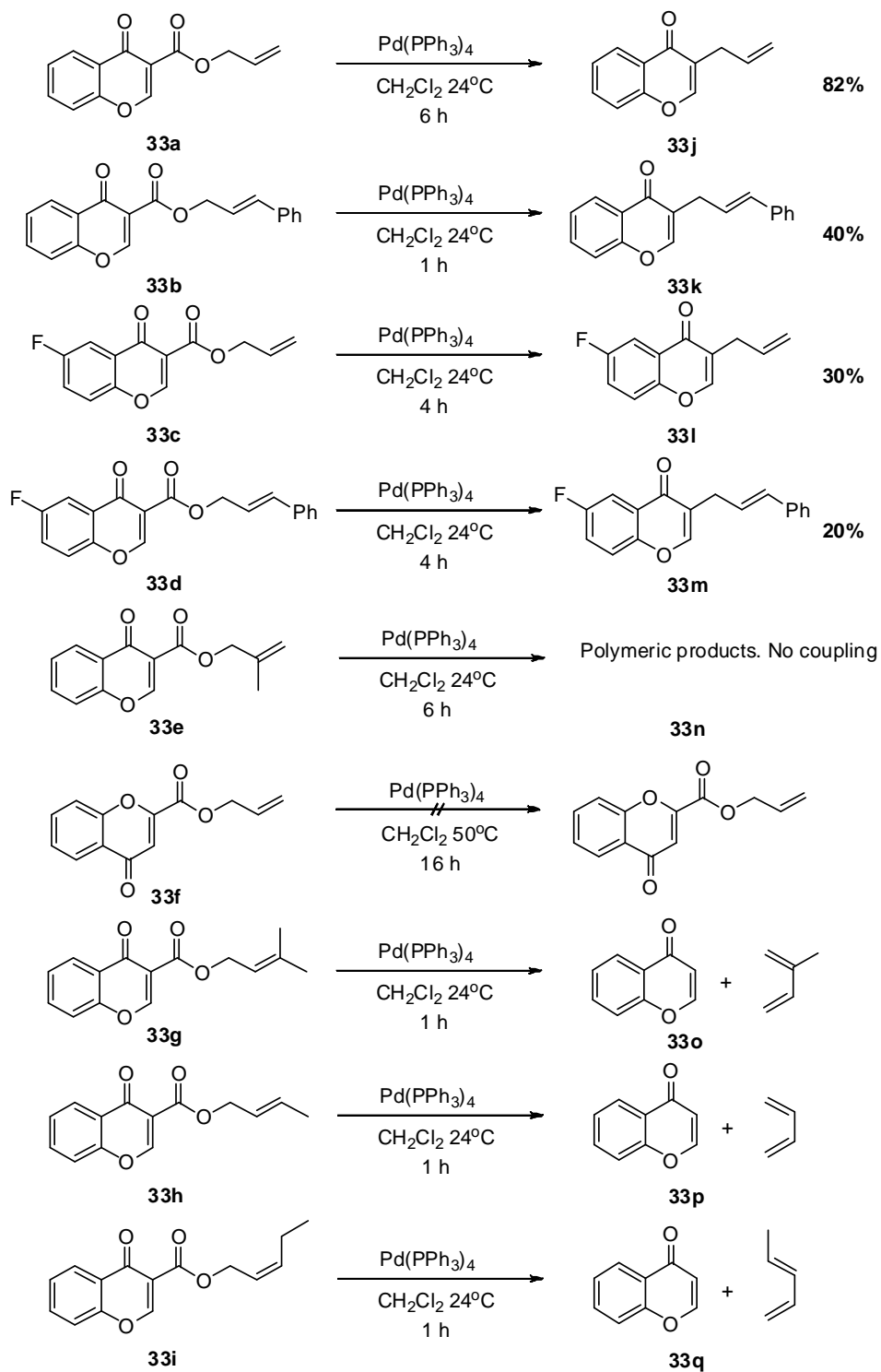
In the interest of exploring the features of the coumarin that allow decarboxylative coupling under such mild conditions, several experiments were performed. First, an acyclic analogue of the coumarin (**32a**) was subjected to the standard reaction conditions for decarboxylative allylation of coumarins, and it did not produce any product. While the reaction with the acyclic derivative failed, pyrone (**32b**) reacts to form the product of decarboxylative coupling (**32e**) under identical conditions to those used in the coumarin coupling.²⁶ Thus, the benzenoid ring of the coumarin is not required for reactivity. Lastly, the analogous thiocoumarin derivative provided coupling product (**32f**) in good yield, showing that the concept of decarboxylative allylation extends to heteroaromatics other than coumarins.

Scheme 32: *Pyrone and thiocoumarin*



Encouraged by the above results, we tried the isomeric chromone and isochromone.

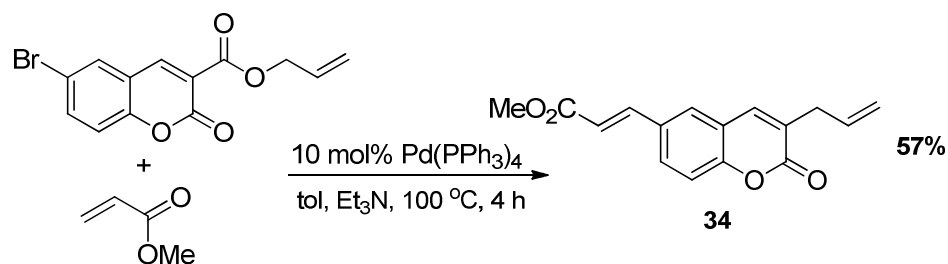
Scheme 33: Chromone and Isochromone



We observe that while the simple allylesters of chromones (**33a-33d**) decarboxylate to give products in poor to moderate yields, presence of any β -hydrogens on the allyl fragments (**33g-33i**) leads to quantitative formation of the protonated product and the corresponding diene. It is also noteworthy, that the isochromone analog (**33f**) undergoes no decarboxylation at all, indicating the necessity of an electronwithdrawing group on the vinyl carbon to achieve the desired decarboxylative coupling.

While decarboxylative couplings are often used in lieu of standard cross-coupling reactions that are more costly or wasteful, decarboxylative couplings are oftentimes complementary to standard palladium-catalyzed coupling reactions. For instance, the decarboxylative sp^2 - sp^3 coupling reported herein can be readily utilized in a tandem decarboxylative allylation/Heck olefination sequence to provide coumarin **34** (Scheme 34).

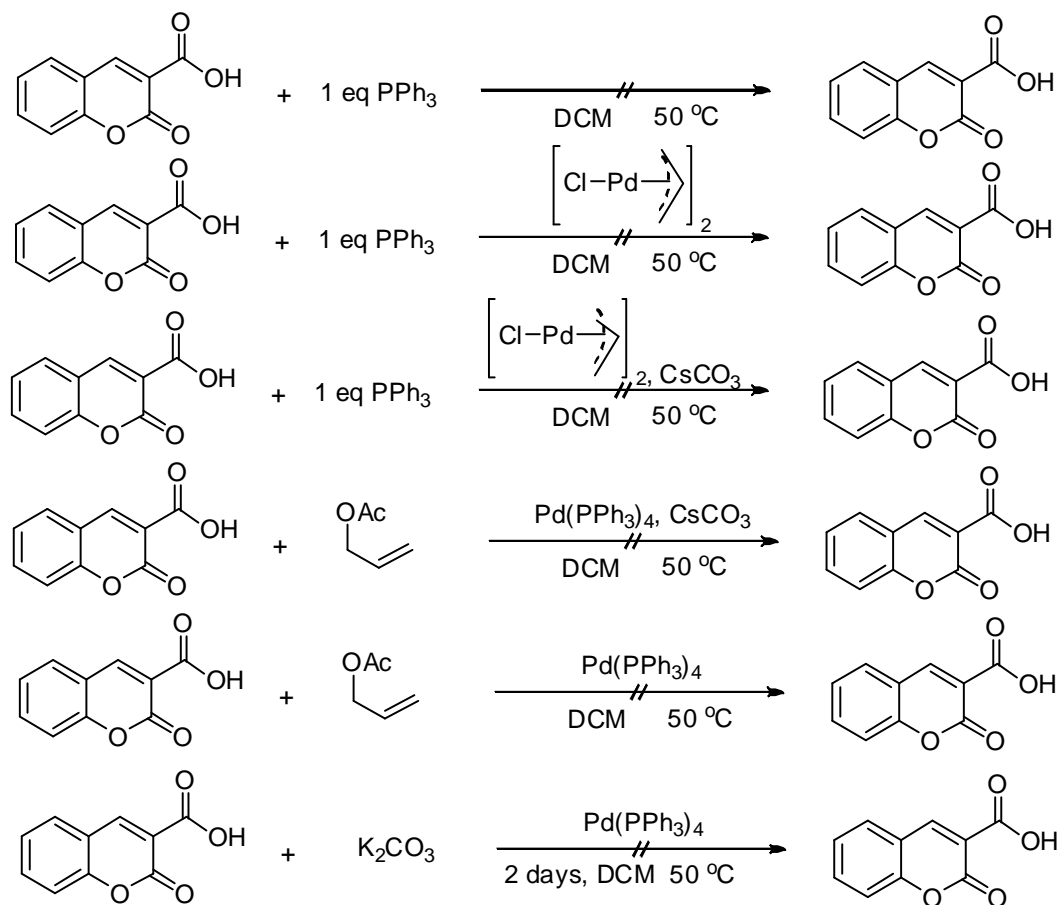
Scheme 34: Decarboxylative coupling/Heck reaction.



3.6 Controls

In order to further probe the mechanism of the reaction, we performed the following experiments to afford a coupling.

Scheme 35: Controls



The above experiments rule out any nucleophile assisted decarboxylation suggested by Corey^{7,8} as discussed earlier.

3.7 Conclusion

In conclusion, we have developed an exceptionally mild decarboxylative sp^2 - sp^3 coupling that results in the allylation of pharmacologically relevant oxygenated heteroaromatics. Continuing studies are aimed at elucidating the mechanism of this transformation in hopes of defining the reasons that decarboxylative couplings of coumarins and related heteroaromatics are so facile.

3.8 Experimental

Materials. Methylene chloride was dried over activated alumina.¹² All reagents were used as received unless otherwise stated. Triethylamine and methyl acrylate were freshly distilled before use. The coumarin 3-allyl ester starting materials were purified by column chromatography and void of any contamination with protic solvents e. g. water or alcohols; the yields of the decarboxylative coupling are highly dependent on the purity of the starting material. ¹H NMR spectra were referenced to residual protio solvent signals. Structural assignments are based on ¹H, ¹³C, DEPT-135, NOESY, and IR spectroscopies.

Preparation of the starting materials: The starting materials were prepared in two steps. In step 1 diallyl malonates were prepared either by acid catalyzed condition (Method A) or by Steglich's conditions (Method B). In step II the diallyl malonates were condensed with the substituted salicylaldehydes to obtain 3-allylcarboxylate-2-chromenones.

Step I, Method A: Preparation of diallyl malonates by acid catalysis:¹³

Malonic acid (1.04 g, 10 mmol), allyl alcohol (3 ml, 44 mmol) and *p*-toluenesulfonic acid monohydrate (0.113 g, 0.6 mmol) were dissolved in benzene (50 mL), and water was removed azeotropically using a Dean-Stark apparatus. After 6 hours the reaction was complete as shown by TLC as well as the calculated amount of water accumulation in the Dean-Stark apparatus. The apparatus was cooled to ambient temperature. The benzene solution was diluted with diethyl ether (50 ml) and washed with saturated aqueous NaHCO₃ (2x15

¹² Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics*, **1996**, 1518-1520.

¹³ Imao, D.; Itoi, A.; Yamazaki, A.; Shirakura, M.; Ohtoshi, R.; Ogata, K.; Ohmori, Y.; Ohta, T.; Ito, Y. *J. Org. Chem.* **2007**, 1652-1658.

mL) brine (15 mL) and dried over anhydrous Na₂SO₄. A yellow liquid remained after evaporation of the solvent under reduced pressure. This residue was purified by flash column chromatography with ethyl acetate/hexane (1:10), to obtain the pure product as yellow oil (1.74 g, 95% yield).

Step 1, Method B: Preparation of diallyl malonates using Steglich's Conditions:¹⁴

Malonic acid (2.2 mmol, 1.1 equiv), DMAP (0.1 equiv) and DCC (2.2 mmol, 1.1 equiv), were successively added to a solution of respective allyl alcohols (2.0 mmol, 1.0 equiv) in dry dichloromethane (10 mL) and the resulting mixture was stirred at room temperature until TLC showed complete consumption of the starting materials. Subsequently, the mixture was filtered and concentrated. Purification of the residue by flash chromatography (ethyl acetate, hexane, 20:80) afforded the pure product of malonate ester.

Step 2: Preparation of 3-allyl carboxylate chromene- 2-one:¹⁵

In a round bottomed flask equipped with a reflux condenser were placed salicylaldehyde (122 mg, 1.0 mmol), diallyl malonate (220 mg, 1.2 mmol) and absolute ethanol (5 mL). To this reaction mixture were added piperidine (100 µL) and glacial acetic acid (5 µL). The reaction mixture was refluxed for 3 hours. After the completion of the reaction was indicated by TLC, the solution was cooled to ambient temperature and the ethanol was evaporated under reduced pressure, diluted with ethyl acetate (10 mL) and washed subsequently with saturated NaHCO₃ (2x5 mL), 1 (N) HCl (5 mL), water (5 mL), brine (5 mL) and dried over anhydrous Na₂SO₄. Evaporation of the solvent under reduced pressure left the crude product which was purified by flash column chromatography (ethyl acetate, hexane, 30:70) to obtain 210 mg pure 3-allyl carboxylate chromene- 2-one (94% yield).

¹⁴ Neises, B.; Steglich, W.; *Organic Syntheses*, **1985**, 63, 183-187.

¹⁵ *Organic Syntheses, Coll. Vol. 3*, p.165 (1955).

3-Allyl carboxylate thiochromene- 2-one was prepared by the modified literature procedure.⁵

General experimental procedure for the decarboxylative sp^2 - sp^3 coupling of coumarin 3-allyl esters:

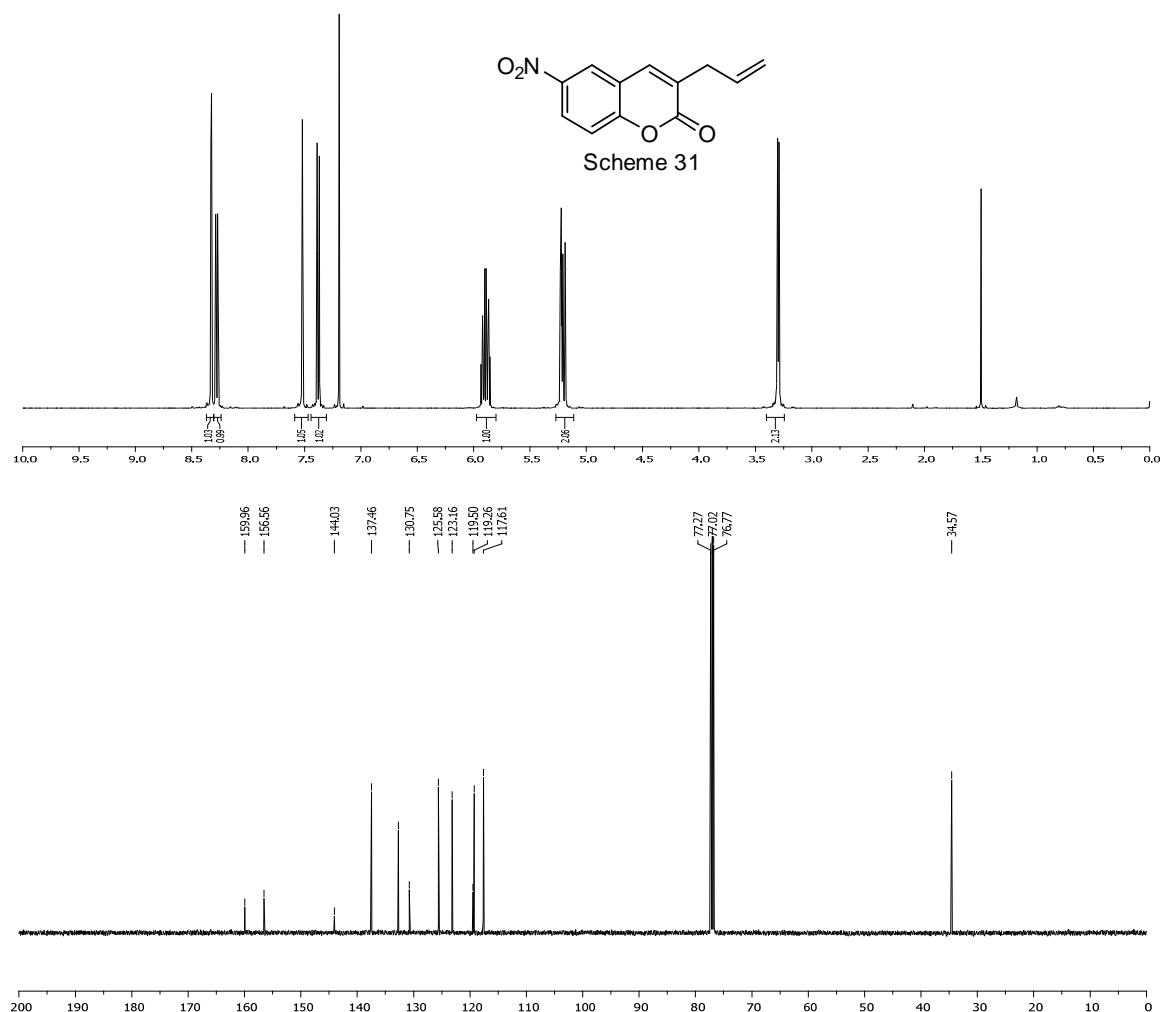
Representative experimental procedure for 3-allyl-6-nitro-2H-chromen-2-one (entry 3, Table 4) A mixture of allyl 6-nitro-2-oxo-2H-chromene-3-carboxylate (**4a**, 110 mg, 0.4 mmol, entry 3, Table 1) and Pd(PPh₃)₄ (46 mg, 10 mol%) was added to a thick-walled reaction tube under argon atmosphere in an inert atmosphere glove box. This mixture was dissolved in dry dichloromethane (6 mL) and heated at 50 °C for 14 h in the sealed tube. After the completion of the reaction was indicated by TLC, the reaction mixture was concentrated under reduced pressure and the residue was purification by flash column chromatography using ethyl acetate, hexane (20:80) to provide 66 mg pure 3-allyl-6-nitro-2H-chromen-2-one (73% yield) as yellowish solid.

The same procedure was followed for all the simple allyl coumarins (Table 1), substituted allyl coumarins (Table 2). The same procedure was followed to produce pyranone, but due to high volatility of the product, dichloromethane was used as an eluent for column chromatography and the solvent was evaporated under a stream of nitrogen in lieu of using reduced pressure. The reaction to produce chromenone was performed at room temperature. For the 3-allyl carboxylate thiochromene- 2-one the reaction was performed at 30 °C.

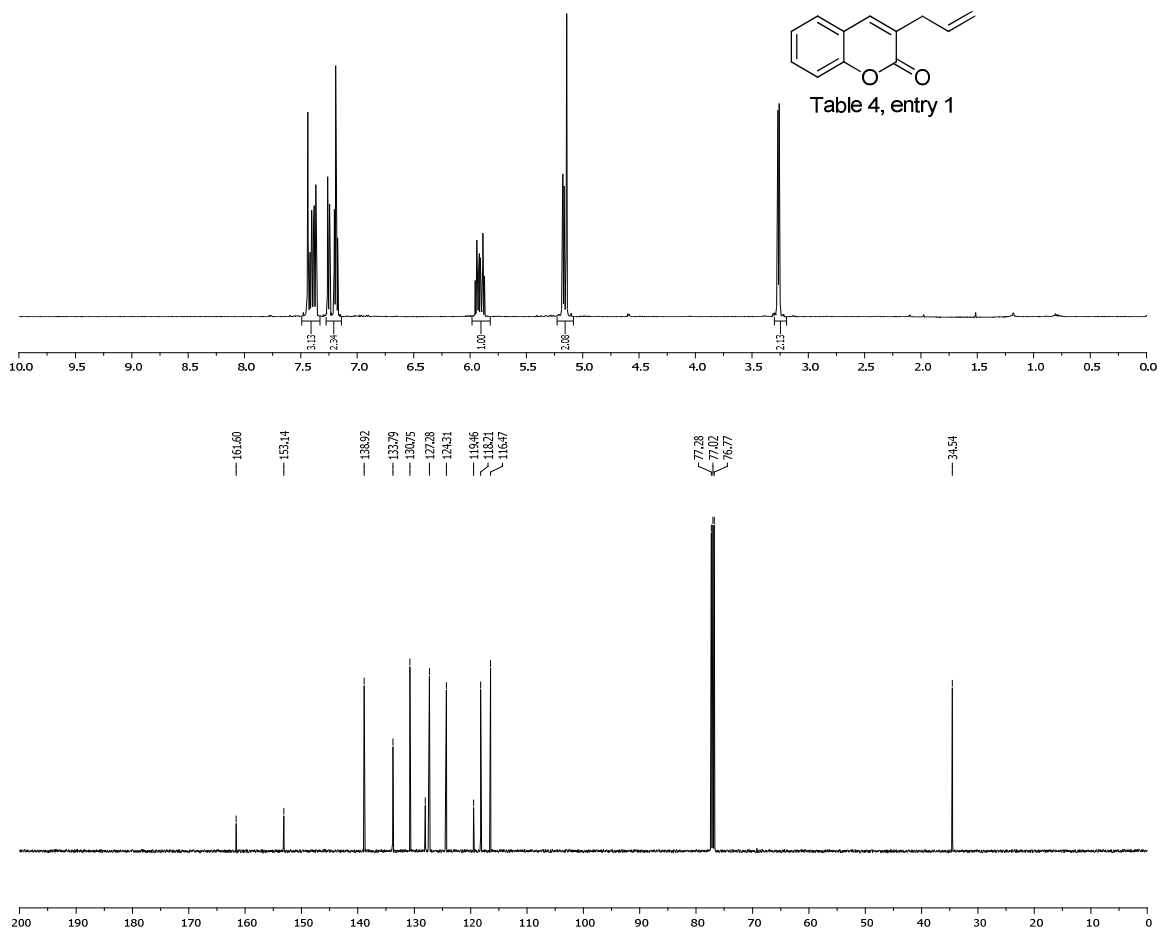
Tandem Heck and sp^2 - sp^3 coupling of allyl-6-bromo-2-oxo-2H-chromene-3-carboxylate (Compound 34):¹⁶

A mixture of allyl 6-bromo-2-oxo-2H-chromene-3-carboxylate (62 mg, 0.20 mmol), freshly distilled methyl acrylate (0.22 mL, 0.40 mmol), triethylamine (0.35 mL, 0.40 mmol), and $Pd(PPh_3)_4$ (23 mg, 0.02 mmol) was placed in a reaction tube under argon in an inert atmosphere glove box and was diluted with toluene (5 mL). The sealed reaction tube was heated at 100 °C for 4 h. After the consumption of the starting materials was indicated by TLC, the reaction mixture was diluted with ethyl acetate (10 mL) and washed with 1(N) HCl (2 mL), water (2 mL), brine (5 mL) and dried over anhydrous Na_2SO_4 . Evaporation of the solvent under reduced pressure left the crude product which was purified by flash column chromatography on silica gel using ethyl acetate/hexane (30:70) eluent. The pure product was isolated as a colourless solid in 57% yield (31 mg).

¹⁶Patel, B. A.; Ziegler, C. B.; Cortese, N. A.; Plevyak, J. E.; Zebovitz, M. T.; Heck, R. F. *J. Org. Chem.* **1977**, 3903-3907.

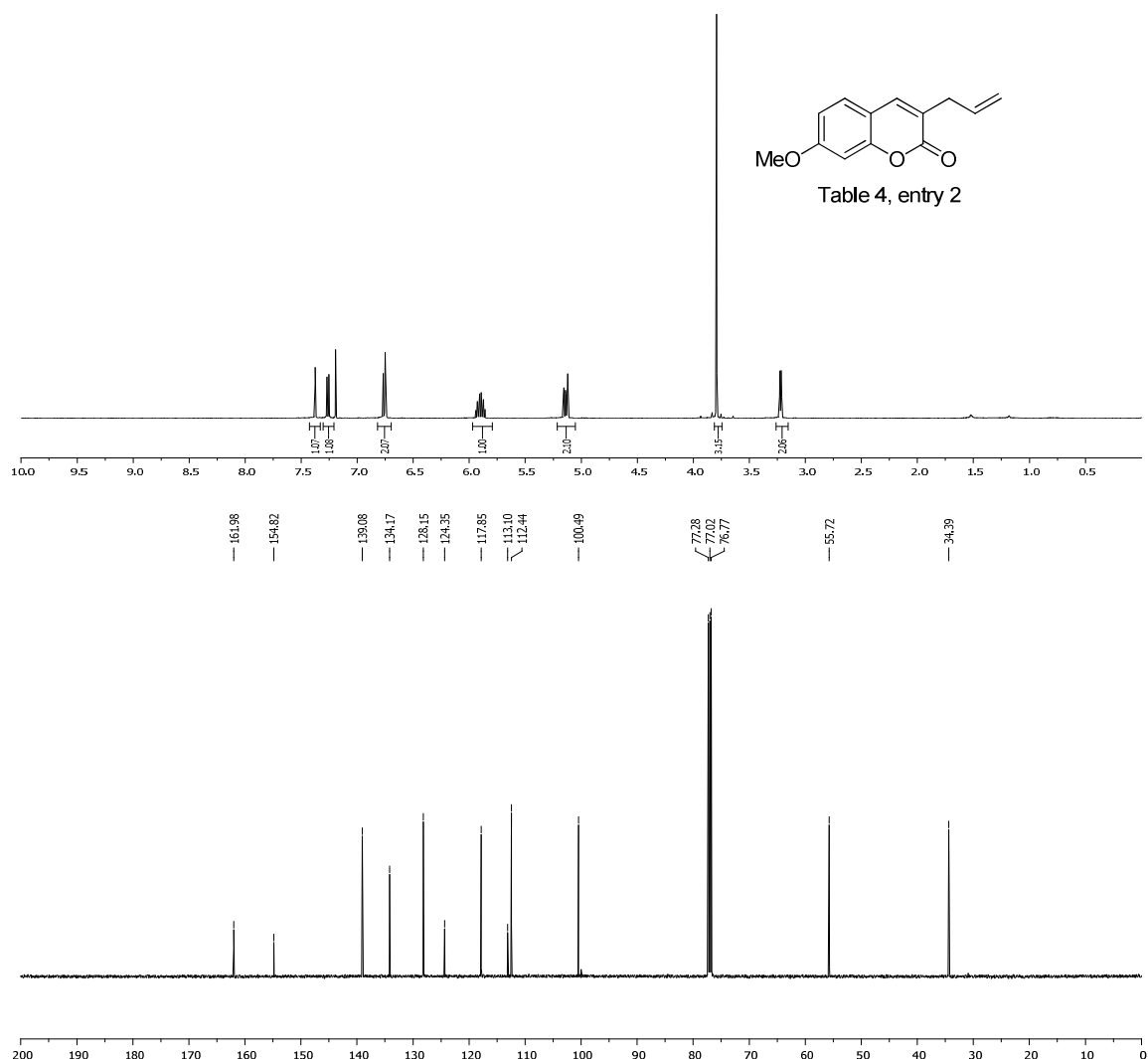


3-Allyl-6-nitro-2H-chromen-2-one (31): Pale yellow solid, m. p. 124 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 8.39 (d, $J = 2.65$ Hz, Ar CH), 8.34 (dd, $J_1 = 6.40$ Hz, $J_2 = 2.65$ Hz, Ar CH), 7.58 (s, C4-H), 7.44 (d, $J = 8.95$ Hz, Ar CH), 5.92-5.97 (m, CH=CH₂), 5.24-5.29 (m, CH=CH₂), 3.36 (dq, $J_1 = 6.75$ Hz, $J_2 = 1.25$ Hz, CH₂-CH=), 3.457 (CH₂-CH=); ¹³C NMR (126 MHz, CDCl₃) δ ppm 159.96 (C=O, quat.), 156.56 (Ar C, quat.), 144.03 (Ar C, quat.), 137.46 (C4-H), 133.25 (CH=CH₂), 130.75 (C3, quat.), 125.58 (Ar CH), 123.16, 119.50 (Ar C, quat.), 119.26 (Ar CH), 117.61 (CH=CH₂), 34.57 (CH₂-CH=); IR (CH₂Cl₂): ν 2962, 1714 (C=O), 1587 (C=C), 1159, 1056, 923 cm⁻¹; Calcd. HRMS for C₁₂H₉NO₄ (M⁺), 231.0532; Found, 231.0529.



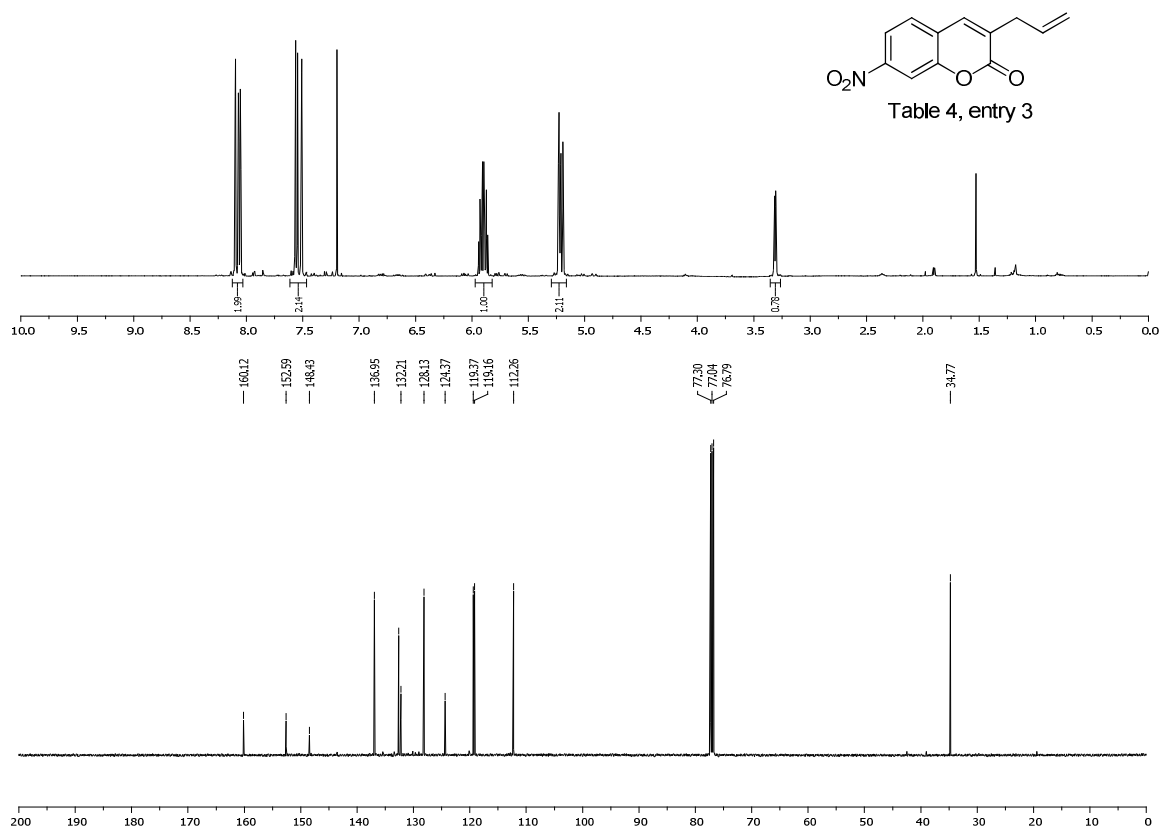
3-Allyl-2H-chromen-2-one (Table 4, entry 1):¹⁷ Colourless solid, m. p. 44 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 7.44 (s, C4-H), 7.36-7.42 (m, 2Ar CH), 7.25 (dd, *J*₁ = 8.35 Hz, *J*₂ = 0.5 Hz, Ar CH), 7.17-7.20 (m, Ar CH), 5.87-5.95 (m, CH=CH₂), 5.14-5.18 (m, CH=CH₂), 3.26 (dq, *J*₁ = 6.75 Hz, *J*₂ = 1.30 Hz, CH₂-CH=); ¹³C NMR (126 MHz, CDCl₃) δ ppm 161.60 (C=O, quat.), 153.14 (Ar C, quat.), 138.92 (C4-H), 133.79 (CH=CH₂), 130.75 (Ar CH), 127.28 (C3, quat.), 124.31 (Ar CH), 119.46 (Ar C, quat.), 118.21 (CH=CH₂), 116.47 (Ar CH), 34.54 (CH₂-CH=); IR (CH₂Cl₂): ν 2925, 1768 (C=O), 1623 (C=C), 1595, 1500, 1454, 1421, 1205, 1127, 1099, 698 cm⁻¹; Calcd. HRMS for C₁₂H₁₀O₂ (M+Na), 209.0578; Found, 209.0573.

¹⁷ Mali, R. S.; Tilve, S. G.; Yeola, S. N.; Manekar, A. R. *Heterocycles*, **1987**, 121-127.



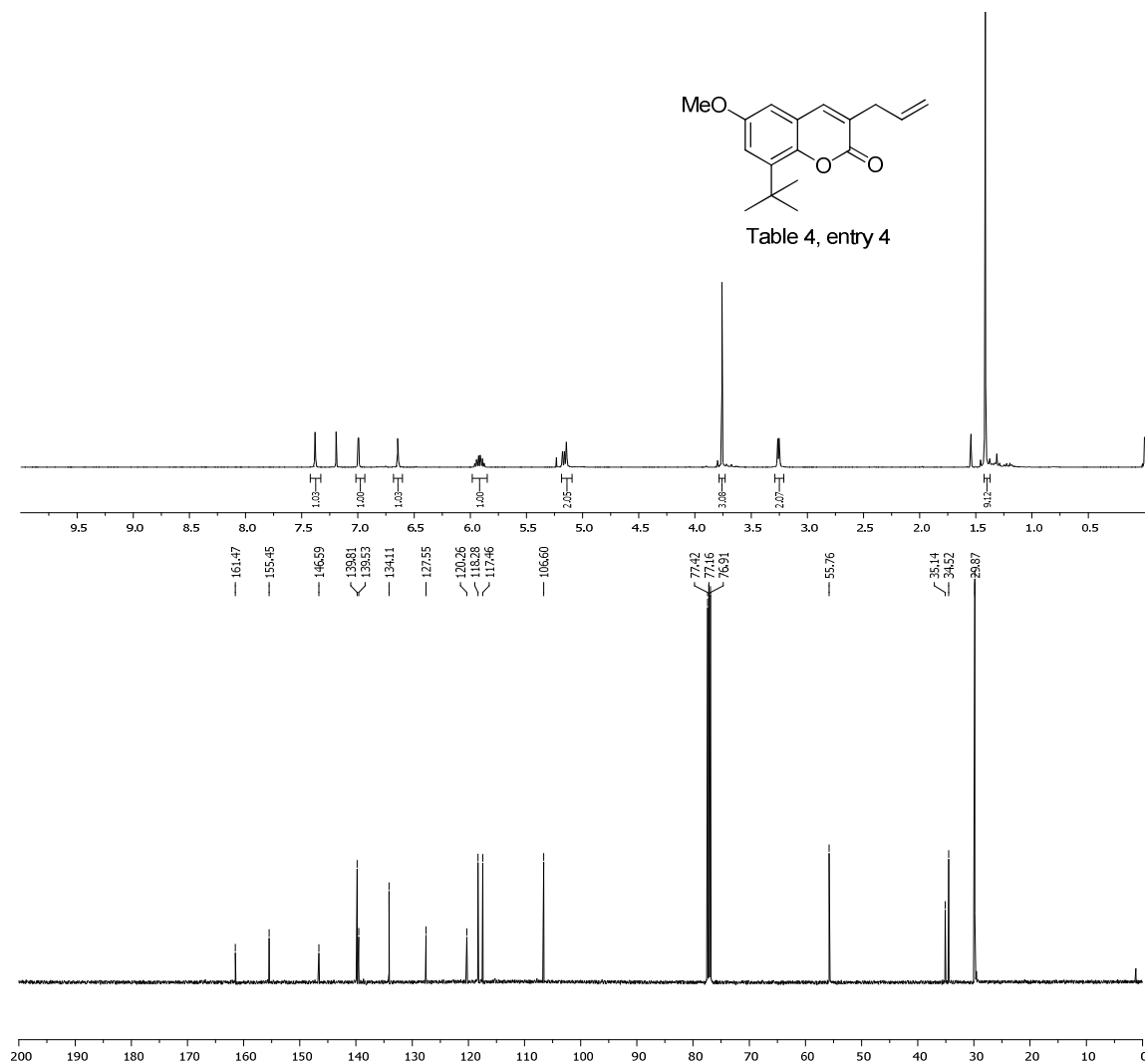
3-Allyl-7-methoxy-2H-chromen-2-one (Table 4, entry 2):¹⁸ Colourless solid, m. p. 54 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 7.44 (s, C4-H), 7.33 (d, *J* = 8.35 Hz, Ar CH), 6.84 (d, *J* = 2.40 Hz, Ar CH), 6.80-6.83 (m, Ar CH), 5.92-6.00 (m, CH=CH₂), 5.18-5.22 (m, CH=CH₂), 3.85 (s, OCH₃), 3.29 (dq, *J*₁ = 6.80 Hz, *J*₂ = 1.25 Hz, CH₂-CH=); ¹³C NMR (126 MHz, CDCl₃) δ ppm 161.97 (C=O, quat.), 161.94 (C7, quat.), 154.82 (Ar C, quat.), 139.08 (C4-H), 134.17 (CH=CH₂), 128.15 (Ar CH), 124.35 (C3, quat.), 117.85 (CH=CH₂), 113.10 (Ar C, quat.), 112.44 (Ar CH), 100.49 (Ar CH), 55.72 (OCH₃), 34.39 (CH₂-CH=); IR (CH₂Cl₂): ν 2962, 1714 (C=O), 1587 (C=C), 1159, 1056, 923 cm⁻¹; Calcd. HRMS for C₁₃H₁₂O₃Na (M+Na), 239.0684; Found, 239.0687.

¹⁸ Mali, R. S.; Tilve, S. G.; eola, S. N.; Manekar, A. R. *Heterocycles*, **1987**, 121-127.

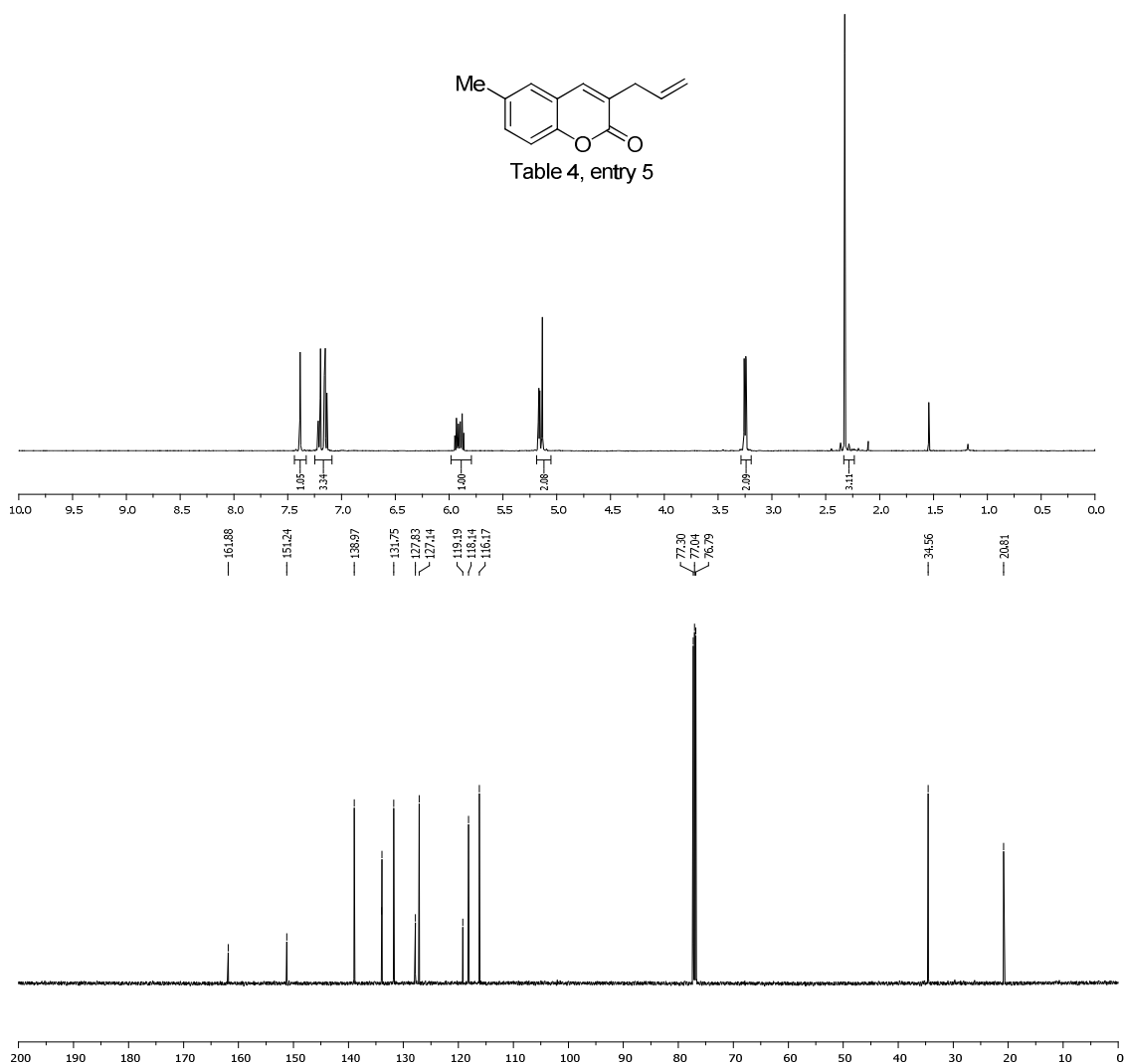


3-Allyl-7-nitro-2H-chromen-2-one (Table 4, entry 3):¹⁹ Pale yellow solid, m. p. 63 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 8.16 (d, *J* = 2.20 Hz, Ar CH), 8.12 (dd, *J*₁ = 6.35 Hz, *J*₂ = 2.20 Hz, Ar CH), 7.62 (d, *J* = 8.50 Hz, Ar CH), 7.57 (s, C4-H), 5.92-6.00 (m, CH=CH₂), 5.24-5.29 (m, CH=CH₂), 3.36 (dq, *J*₁ = 6.80 Hz, *J*₂ = 1.25 Hz, CH₂-CH=); ¹³C NMR (126 MHz, CDCl₃) δ ppm 160.12 (C=O, quat.), 152.99 (Ar C, quat.), 148.43 (Ar C, quat.), 136.95 (C4-H), 132.64 (Ar CH), 132.21 (Ar C, quat.), 128.13 (CH=CH₂), 124.37 (C3, quat.), 119.37 (Ar CH), 119.16 (CH=CH₂), 112.26 (Ar CH), 34.77 (CH₂-CH=); IR (CH₂Cl₂): ν 2962, 1712 (C=O), 1565 (C=C), 1161, 1057, 926, 755 cm⁻¹; Calcd. HRMS for C₁₂H₉NO₄ (M⁺), 231.0532; Found, 231.0537.

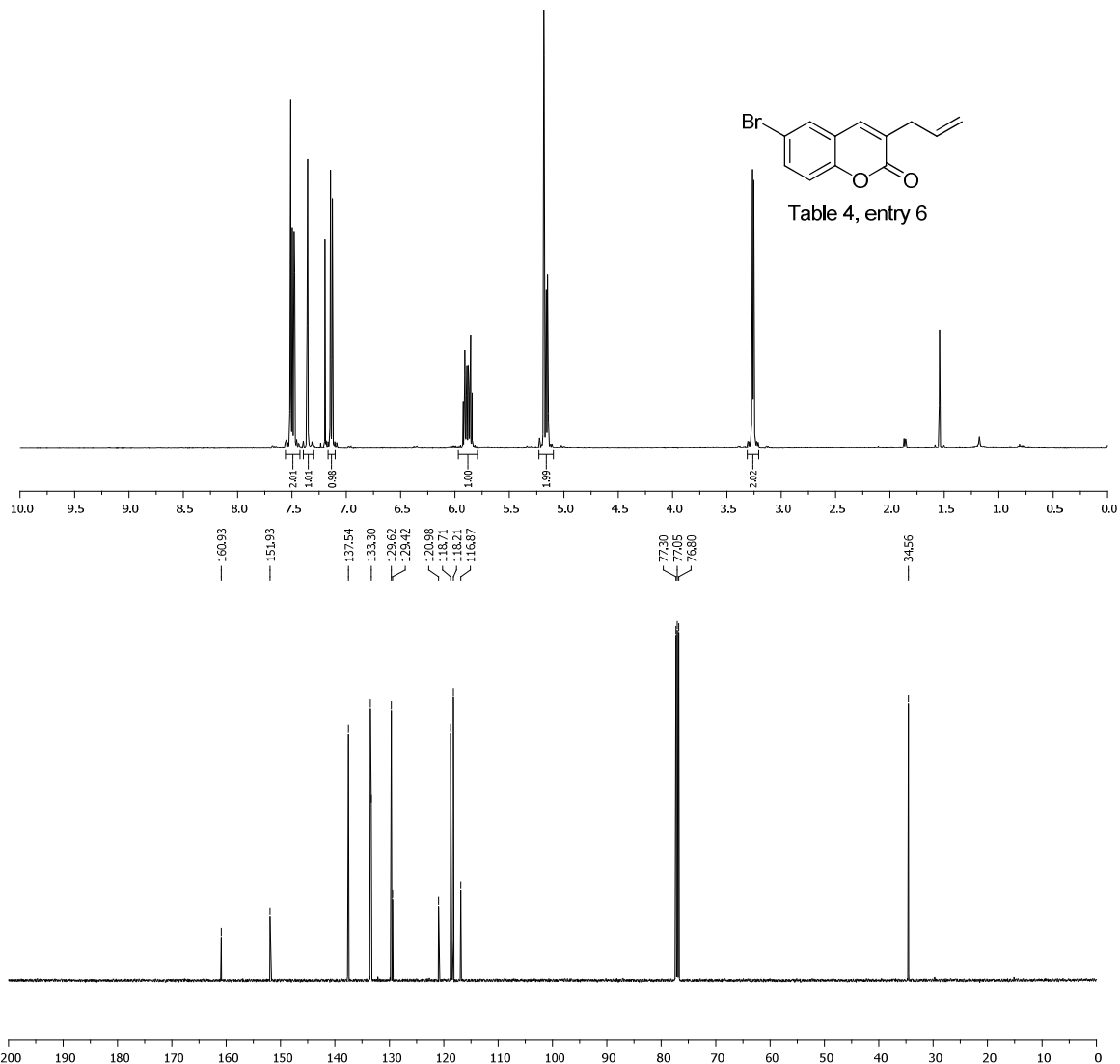
¹⁹ Black, M.; Cadogan, J. I. G.; McNab, H.; MacPherson, A. D.; Roddam, V. P. Smith, C.; Swenson, H. R. *J. Chem. Soc. Perkin Trans. 1*, **1997**, 2483-2493.

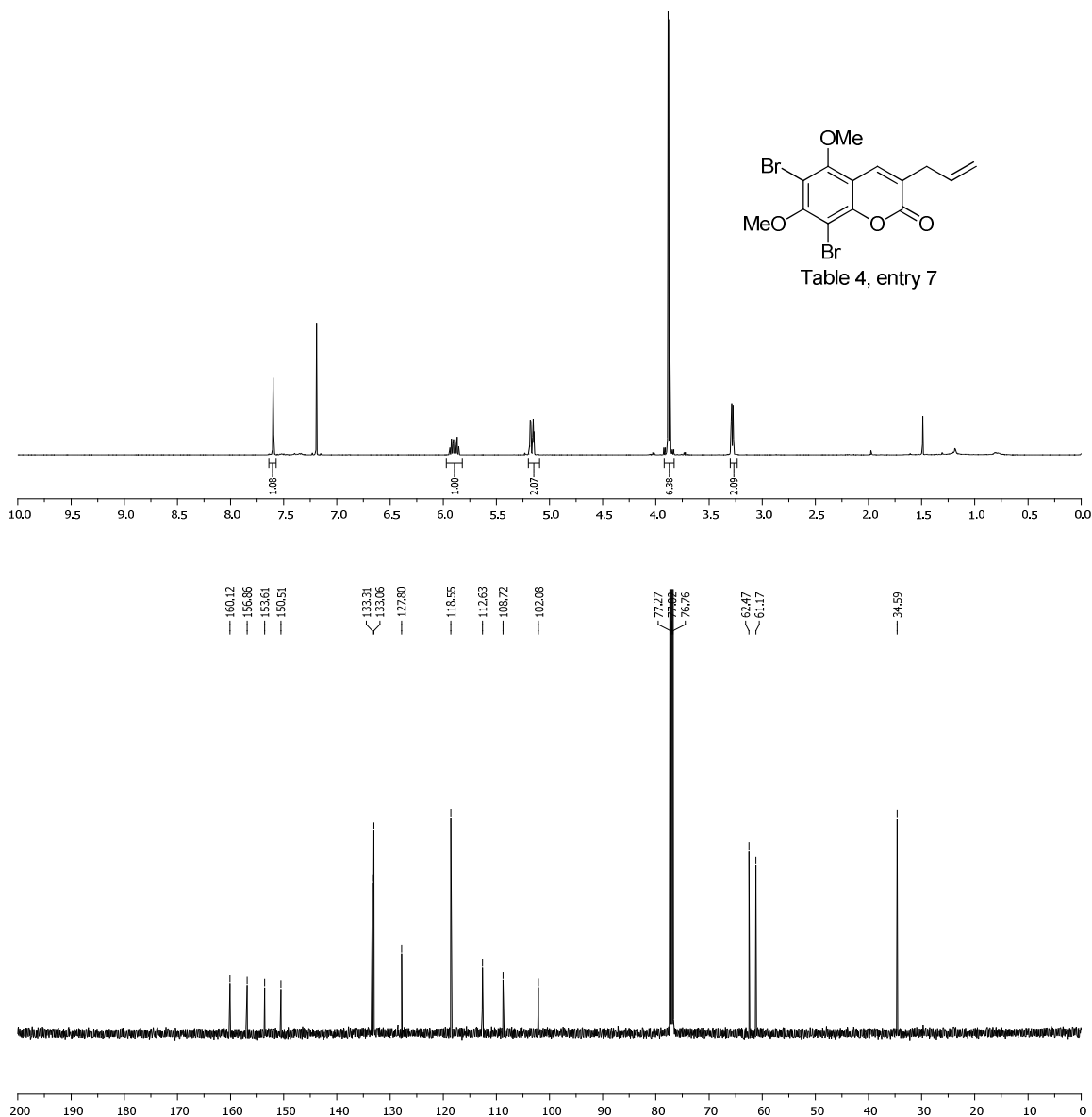


3-Allyl-8-*tert*-butyl-6-methoxy-2H-chromen-2-one (Table 4, entry 4): Off-white solid, m. p. 95 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 7.44 (s, C4-H), 7.06 (d, *J* = 3.00 Hz, C5-H), 6.71 (d, *J* = 3.00 Hz, C7-H), 5.94-6.01 (m, CH₂-C=H), 5.21-5.24 (m, HC=CH₂), 3.32 (dd, *J*₁ = 6.80 Hz, *J*₂ = 1.25 Hz, CH₂-C=H); ¹³C NMR (126 MHz, CDCl₃) δ ppm 161.47 (C=O), 155.45 (C6, quat.), 146.99 (C8, quat), 139.81 (C4), 139.53 (C9, quat.), 134.11 (CH₂=CH), 127.55 (C10, quat.), 120.26 (C3, quat.), 118.28 (CH=CH₂), 117.46 (C7), 106.60 (C5), 55.76 (OCH₃), 35.14 (CCH₃, quat.), 32.85 (CH-CH₂), 28.20 (CCH₃); IR (CH₂Cl₂): ν 2962, 1714 (C=O), 1587 (C=C), 1461, 1434, 1159, 1056, 1027, 1002, 757 cm⁻¹; Calcd. HRMS for C₁₇H₂₀O₃Na (M+Na), 295.1316; Found, 295.1297.



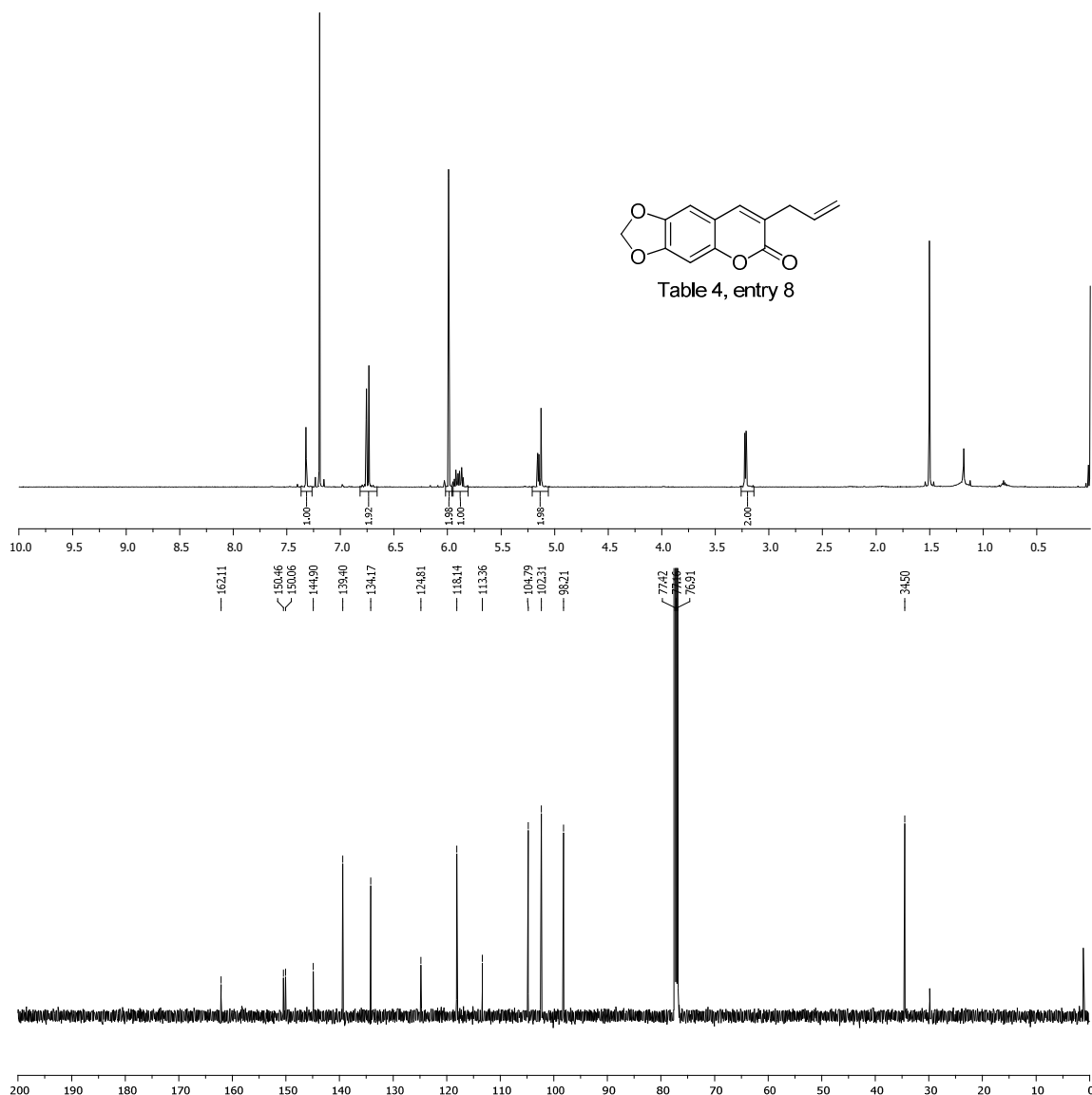
3-Allyl-6-methyl-2H-chromen-2-one (Table 4, entry 5): Colourless solid, m. p. 39 °C; ^1H NMR (500 MHz, CDCl_3) δ ppm 7.51 (s, C4-H), 7.32-7.34 (m, 2ArCH), 7.26-7.29 (m, 2ArCH), 5.99-6.06 (m, $\text{CH}_2\text{-C}=\text{H}$), 5.25-5.30 (m, $\text{HC}=\text{CH}_2$), 3.37 (dd, $J_1 = 6.80$ Hz, $J_2 = 1.25$ Hz, $\text{CH}_2\text{-C}=\text{H}$), 2.45 (s, ArCH₃); ^{13}C NMR (126 MHz, CDCl_3) δ ppm 161.88 ($\text{C}=\text{O}$), 151.24 (C6, quat.), 138.97 (C4), 133.96 (C9, quat.), 133.91 ($\text{CH}_2=\text{CH}$), 131.75 (C8), 127.82 (C10, quat.), 127.14 (C5), 119.19 (C3, quat.), 118.18 ($\text{CH}=\text{CH}_2$), 116.17 (C7), 34.56 (CH-CH_2), 20.81 (ArCH₃); IR (CH_2Cl_2): ν 2965, 1708 ($\text{C}=\text{O}$), 1582 ($\text{C}=\text{C}$), 1466, 1432, 1159, 1056, 1027, 957 cm^{-1} ; Calcd. HRMS for $\text{C}_{17}\text{H}_{20}\text{O}_3\text{Na}$ ($\text{M}+\text{Na}$), 223.0735; Found, 223.0728.



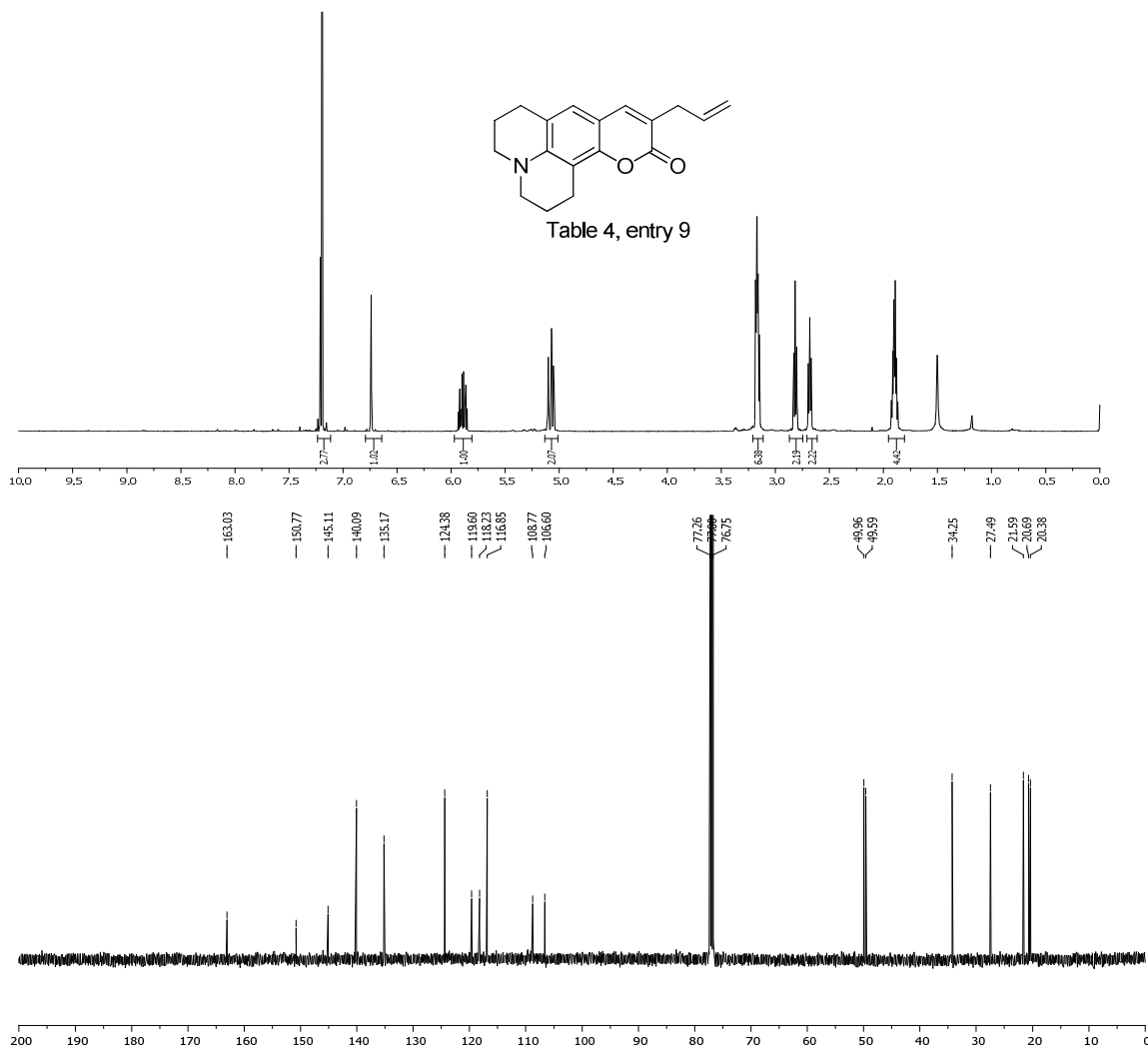


3-Allyl-6,8-dibromo-5,7-dimethoxy-2H-chromen-2-one (Table 4, entry 7):

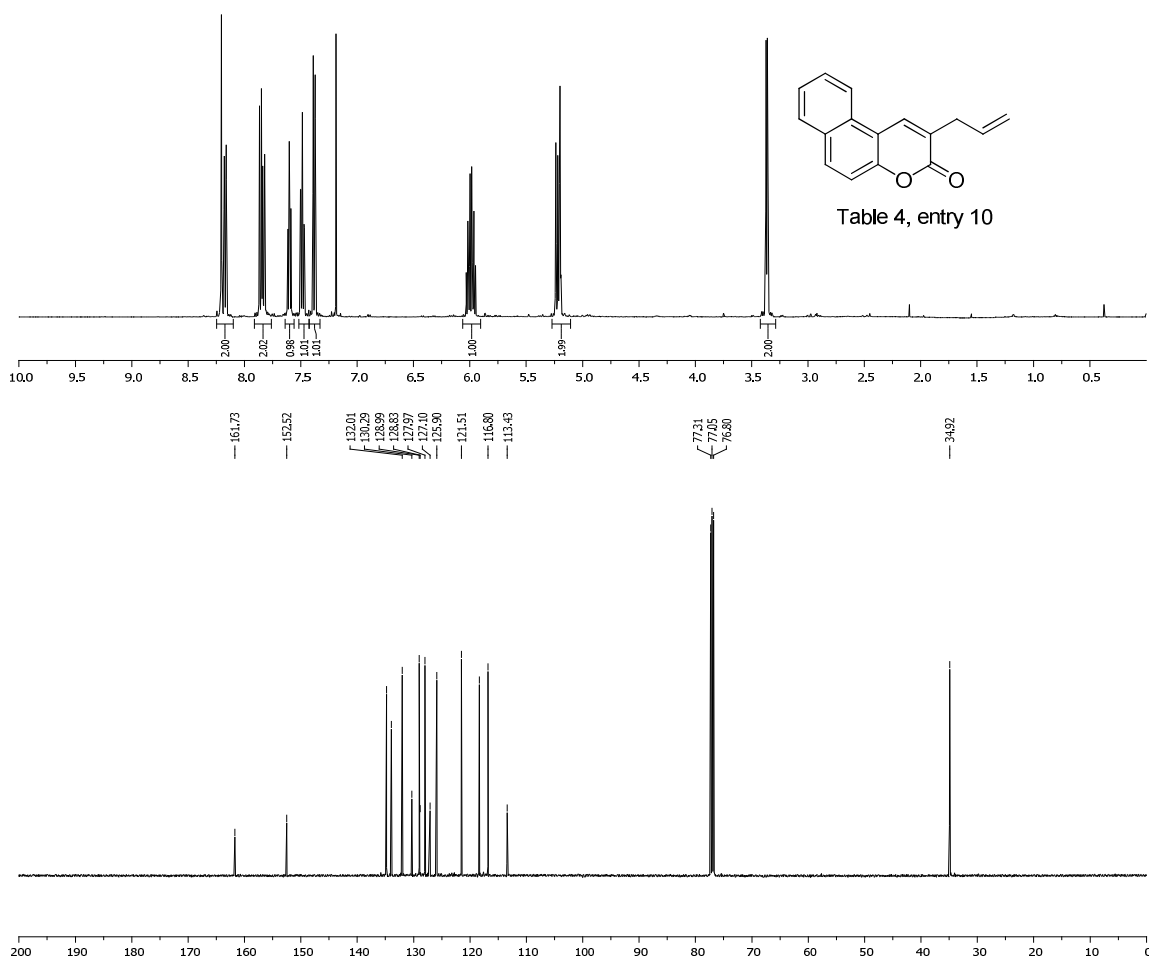
Pale yellow solid, m. p. 92 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 7.66 (t, *J* = 1.25 Hz, C4-H), 5.92-6.00 (m, CH₂-C=H), 5.21-5.25 (m, HC=CH₂), 3.95 (s, OCH₃), 3.93 (s, OCH₃), 3.35 (dq, *J*₁ = 6.65 Hz, *J*₂ = 1.25 Hz, CH₂-C=H); ¹³C NMR (126 MHz, CDCl₃) δ ppm 160.12 (C=O), 156.86 (Ar C, quat.), 153.61 (Ar C, quat.), 150.50 (Ar C, quat.), 133.31 (Ar CH), 133.68 (C4), 133.06 (CH₂=CH), 127.80 (C3, quat.), 118.54 (CH=CH₂), 112.63 (Ar C, quat.), 108.72 (Ar C, quat.), 102.07 (Ar C, quat.), 62.47 (OCH₃), 61.16 (OCH₃), 34.55 (CH-CH₂); IR (CH₂Cl₂): ν 2965, 1708 (C=O), 1586 (C=C), 1376, 1147, 1135, 1076, 966 cm⁻¹; Calcd. HRMS for C₁₄H₁₂Br₂O₄Na (M+Na), 424.9000; Found, 424.9013.



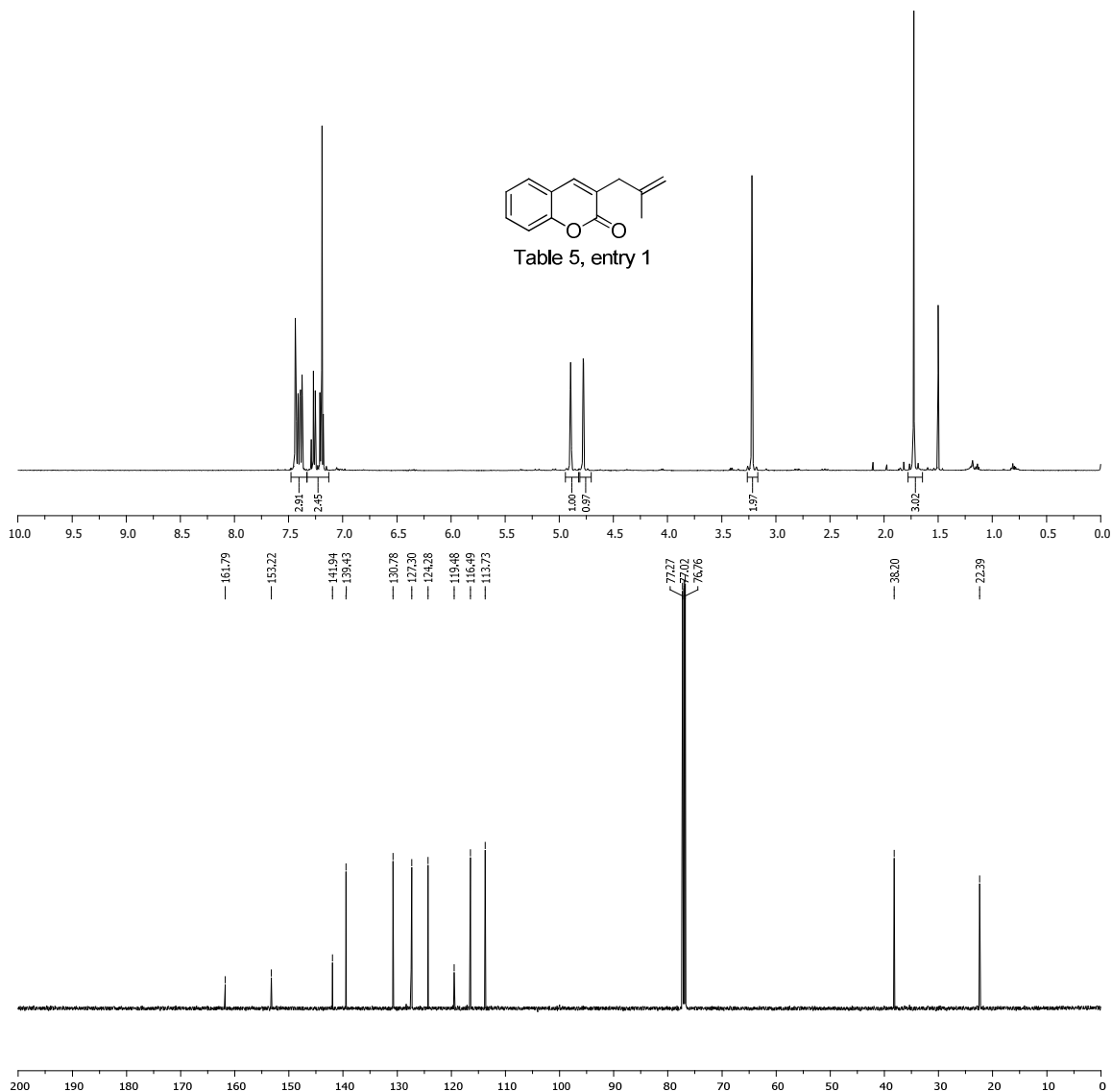
7-Allyl-6H-[1,3]dioxolo[4,5-g]chromen-6-one (Table 4, entry 8): Colourless solid, m. p. 135 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 7.39 (s, C4-H), 6.82 (s, C5-H), 6.80 (s, C8-H), 6.06 (s, O-CH₂-O), 5.92-5.98 (m, CH₂-C=H), 5.19-5.23 (m, HC=CH₂), 3.28 (dq, *J*₁ = 6.80 Hz, *J*₂ = 1.25 Hz, CH₂-C=H); ¹³C NMR (126 MHz, CDCl₃) δ ppm 162.11 (C=O, quat.), 150.46 (Ar C, quat.), 153.06 (Ar C, quat.), 144.90 (Ar C, quat.), 139.40 (C4-H), 134.17 (CH₂=CH), 124.81 (C3), 118.14 (CH=CH₂), 113.36 (Ar C, quat.), 104.79 (Ar CH), 102.31 (O-CH₂-O), 98.21 (Ar CH), 34.50 (CH-CH₂); IR (CH₂Cl₂): ν 2968, 1708 (C=O), 1593 (C=C), 1376, 1147, 1135, 1076, 966 cm⁻¹; Calcd. HRMS for C₁₃H₁₁O₄ (M+H), 231.0657; Found, 231.0663.



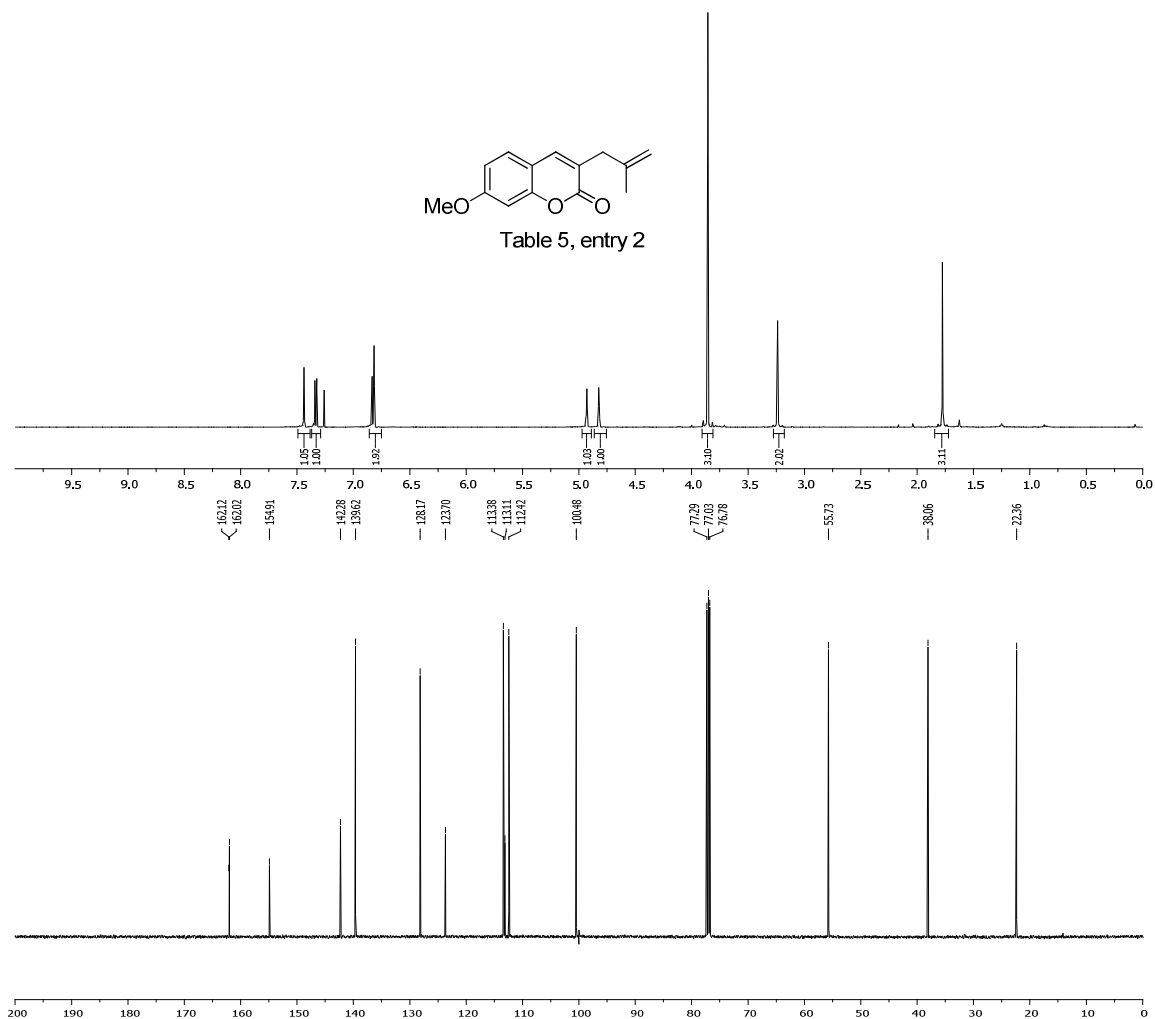
3-Allyl-6,7,8-(2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizine)-2H-chromen-2-one (Table 4, entry 9): Pale yellow solid, m. p. 67 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 7.27 (t, *J* = 0.95 Hz, C4-H), 6.80 (s, C5-H), 5.91-5.99 (m, CH₂-C=H), 5.11-5.17 (m, HC=CH₂), 3.21-3.25 (m, 2N-CH₂, CH₂=CH), 2.88 (t, *J* = 6.60 Hz, N-CH₂-CH₂-CH₂), 2.74 (t, *J* = 6.10 Hz, N-CH₂-CH₂-CH₂), 1.93-1.99 (m, 2N-CH₂-CH₂-CH₂); ¹³C NMR (126 MHz, CDCl₃) δ ppm 163.03 (C=O, quat.), 150.77 (Ar C, quat.), 145.11 (Ar C, quat.), 140.09 (Ar CH), 135.17 (CH₂=CH), 124.37 (C4), 119.59 (C3, quat.), 118.23 (Ar C, quat.), 116.85 (CH=CH₂), 108.77 (Ar C, quat.), 106.60 (Ar C, quat.), 49.96 (N-CH₂), 49.59 (N-CH₂), 34.25 (CH=CH₂), 27.49 (N-CH₂-CH₂-CH₂), 21.59 (N-CH₂-CH₂-CH₂), 20.69 (N-CH₂-CH₂-CH₂-CH₂), 20.38 (N-CH₂-CH₂-CH₂); IR (CH₂Cl₂): ν 1704 (C=O), 1608 (C=C), 1566, 1512, 1309, 1164 cm⁻¹; Calcd. HRMS for C₁₈H₁₉O₂ (M⁺), 281.1416; Found, 281.1421.



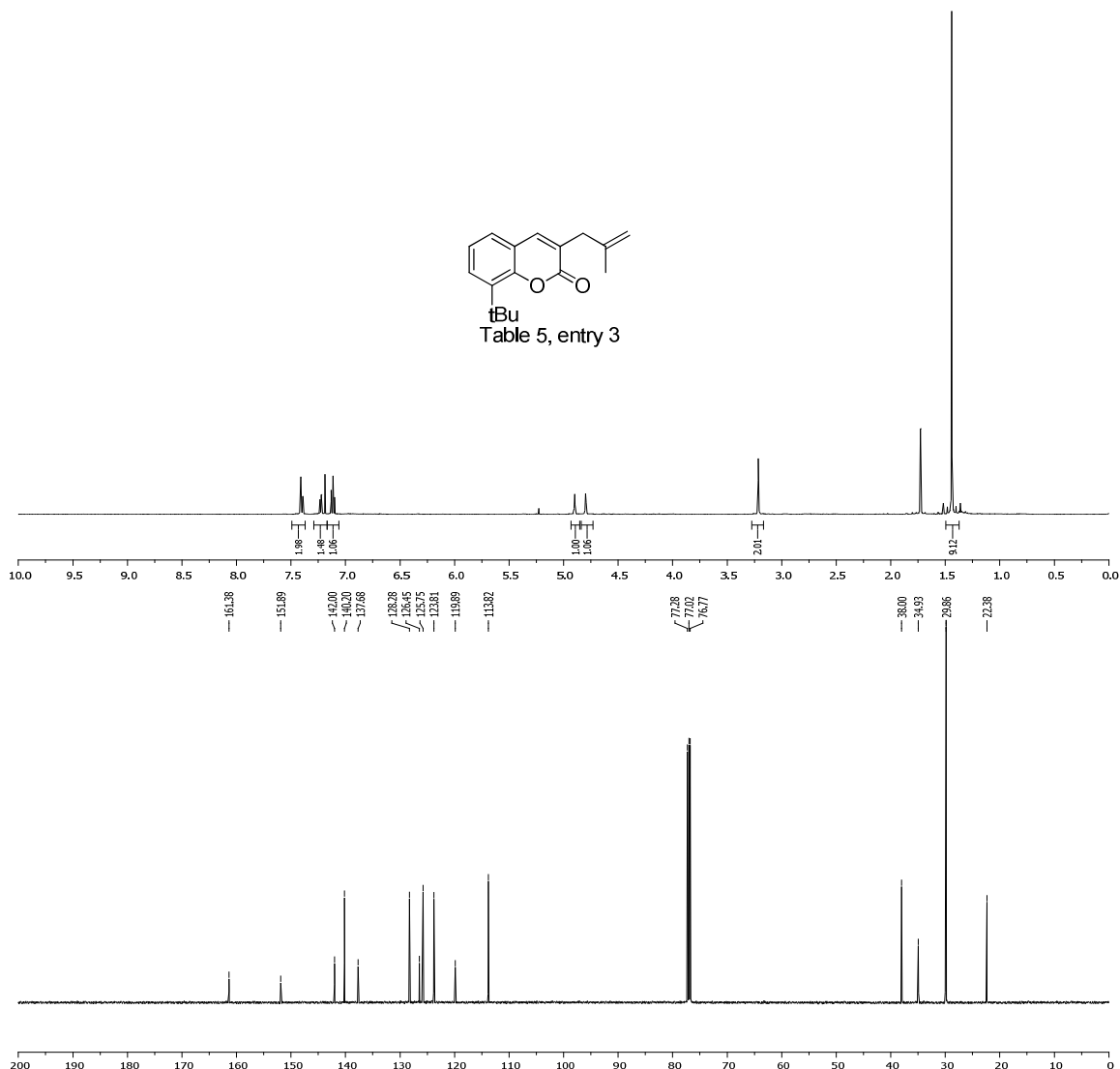
2-Allyl-3H-benzo[f]chromen-3-one (Table 4, entry 10): Pale yellow solid, m. p. 89 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 8.38 (s, C4-H), 8.24 (d, J = 8.35 Hz, Ar CH), 7.92 (d, J = 9.00 Hz, Ar CH), 7.90 (d, J = 8.20 Hz, Ar CH), 7.65-7.68 (m, Ar CH), 7.54-7.57 (m, Ar CH), 7.45 (d, J = 9.00 Hz, Ar CH), 6.02-6.10 (m, CH₂-C=H), 5.26-5.31 (m, HC=CH₂), 3.44 (dq, J₁ = 5.70 Hz, J₂ = 1.30 Hz, CH₂-C=H); ¹³C NMR (126 MHz, CDCl₃) δ ppm 161.73 (C=O, quat.), 152.52 (Ar C, quat.), 134.83 (Ar CH), 133.93 (C4), 132.01 (Ar CH), 130.29 (Ar C, Quat.), 128.99 (CH₂=CH), 128.83 (Ar C, quat.), 127.97 (Ar CH), 127.10 (C3, quat.), 125.90 (Ar CH), 121.51 (Ar CH), 118.37 (CH=CH₂), 116.80 (Ar CH), 113.43 (Ar C, quat.) 34.91 (CH-CH₂); IR (CH₂Cl₂): ν 2964, 1712 (C=O), 1586 (C=C), 1376, 1159, 1135, 1076, 961, 755 cm⁻¹; Calcd. HRMS for C₁₆H₁₃O₂ (M+H), 237.0916; Found, 237.0921.



3-(2-Methylallyl)-2H-chromen-2-one (Table 5, entry 1): Colorless solid, m. p. 43 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 7.51(s, C4-H), 7.45-7.50 (m, 2Ar CH), 7.33 (dd, *J*₁ = 7.70 Hz, *J*₂ = 0.45 Hz, Ar CH), 7.25-7.28 (m, Ar CH), 4.97 (t, *J* = 1.65 Hz, CH₂-CH(CH₃)=CH), 4.85 (q, *J* = 0.95 Hz, CH(CH₃)=CH), 3.22 (s, CH₂-CH(CH₃)), 1.73 (s, C-CH₃); ¹³C NMR (126 MHz, CDCl₃) δ ppm 161.79 (C=O, quat.), 153.22 (Ar C, quat.), 141.94 (C(CH₃)=CH₂ quat.), 130.78 (Ar CH), 127.43 (Ar CH), 127.29 (Ar C, quat.), 124.28 (Ar CH), 119.48 (Ar C, quat.), 116.49 (Ar CH), 113.73 (C(CH₃)=CH₂), 38.20 (CH₂-C(CH₃)), 22.39 (C-CH₃); IR (CH₂Cl₂): ν 1716 (C=O), 1608 (C=C), 1456, 1421, 1168, 1054, 754 cm⁻¹; Calcd. HRMS for C₁₃H₁₃O₂ (M+H), 201.0916; Found, 201.0923.

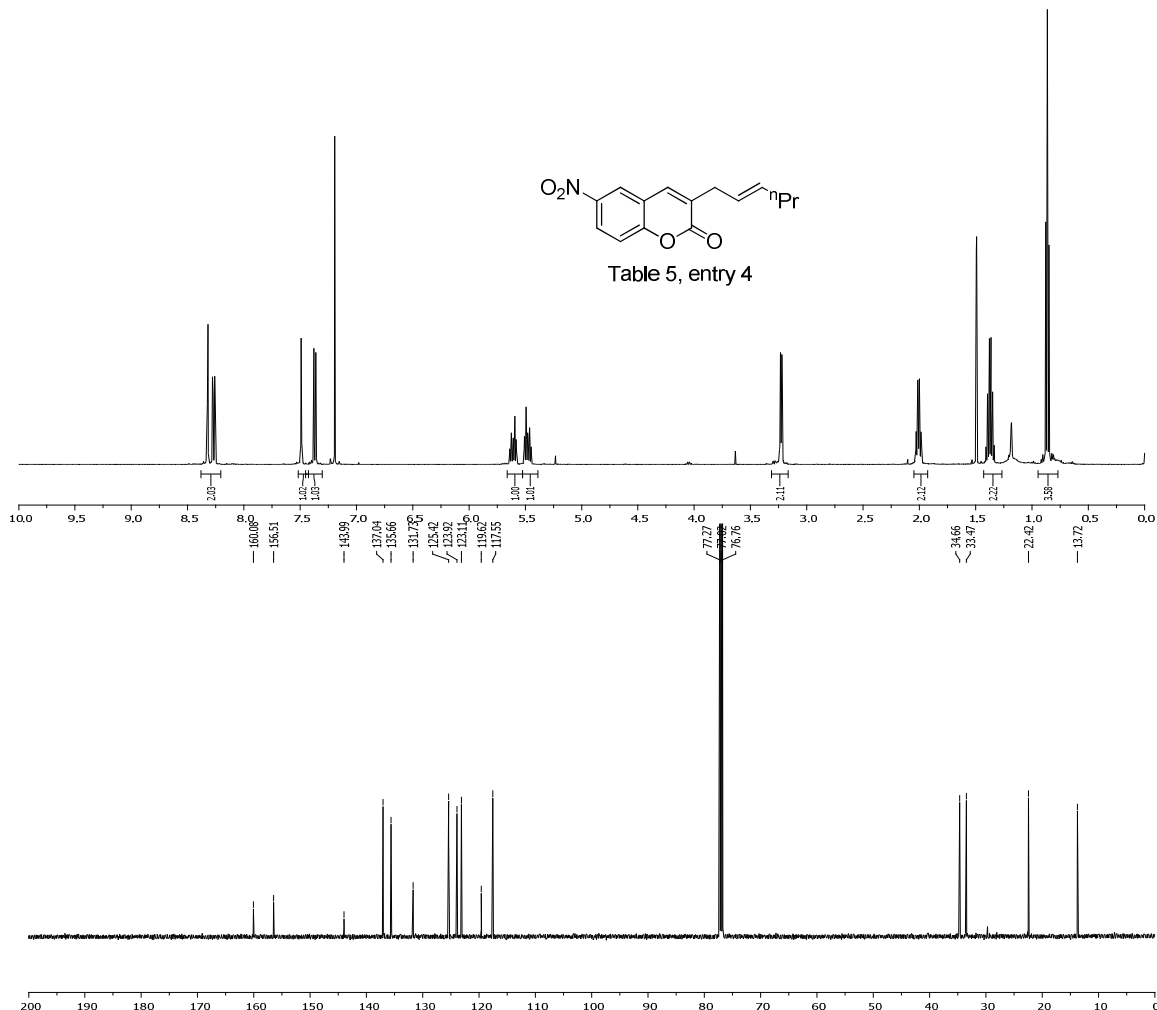


7-Methoxy-3-(2-methylallyl)-2H-chromen-2-one (Table 5, entry 2): Colorless solid, m. p. 76 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 7.44 (s, C4-H), 7.33 (d, *J* = 8.35 Hz, C5-H), 6.83 (d, *J* = 2.5 Hz, C6-H), 6.81-6.82 (m, C8-H), 4.93 (t, *J* = 1.65 Hz, CH₂-CH(CH₃)=CH), 4.86 (q, *J* = 0.95 Hz, CH(CH₃)=CH), 3.85 (s, OCH₃), 3.23 (s, CH₂-CH(CH₃)), 1.77 (s, C-CH₃); ¹³C NMR (126 MHz, CDCl₃) δ ppm 162.12 (C=O), 162.02 (C7, quat.), 154.91 (Ar C, quat.), 142.28 (C(CH₃)=CH₂, quat.), 139.62 (C4), 128.17 (Ar CH), 123.69 (Ar C, quat.), 113.38 (Ar CH), 113.11 (Ar C), 112.42 (Ar CH), 100.48 (C(CH₃)=CH₂), 55.72 (OCH₃), 38.23 (CH₂-C(CH₃)), 22.65 (C-CH₃); IR (CH₂Cl₂): ν 1714 (C=O), 1587 (C=C), 1431, 1164, 1068, 755 cm⁻¹; Calcd. HRMS for C₁₄H₁₄O₃Na (M+Na), 253.0841; Found, 253.0832.

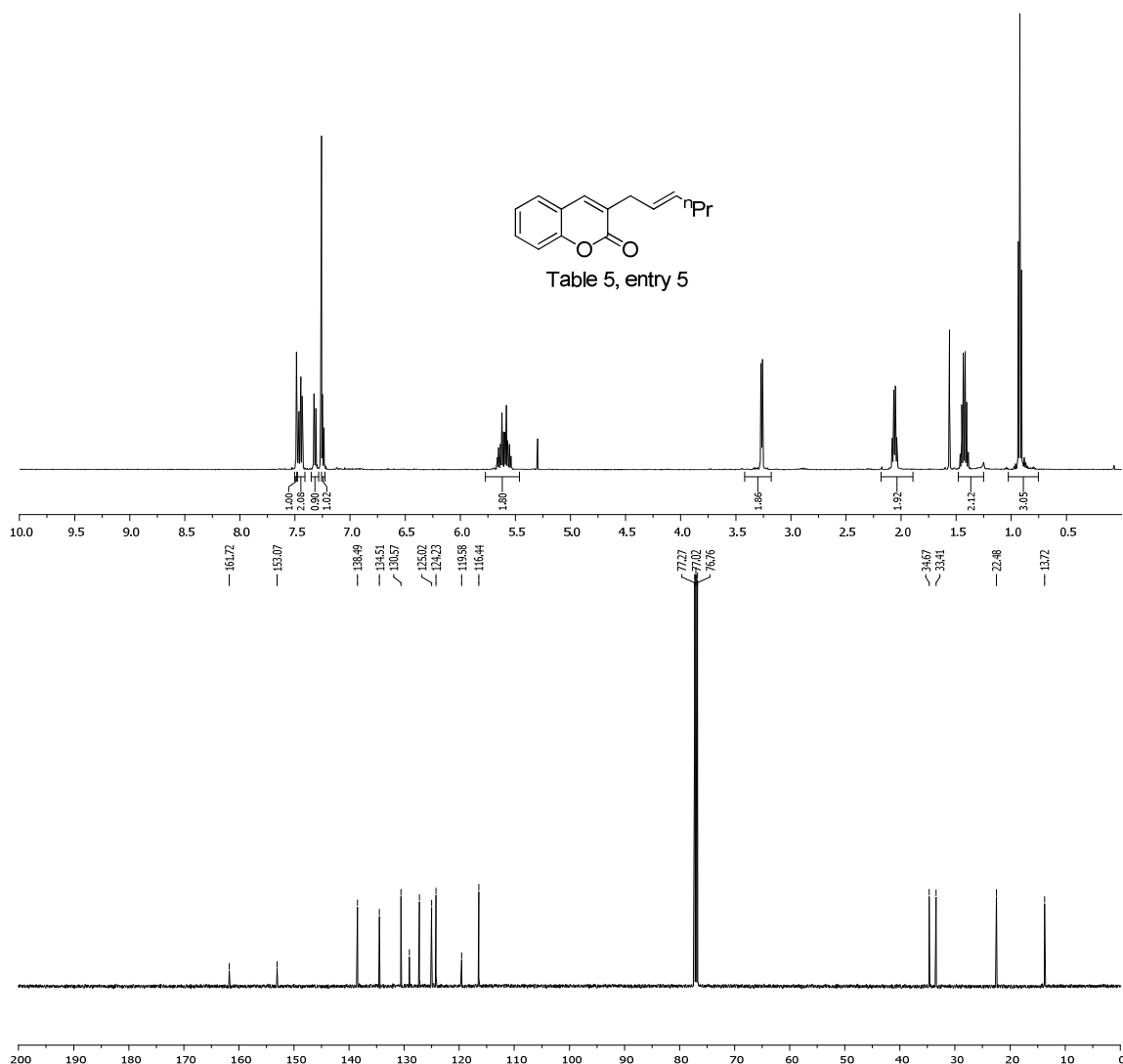


8-*tert*-Butyl-3-(2-methylallyl)-2H-chromen-2-one (Table 5, entry 3):

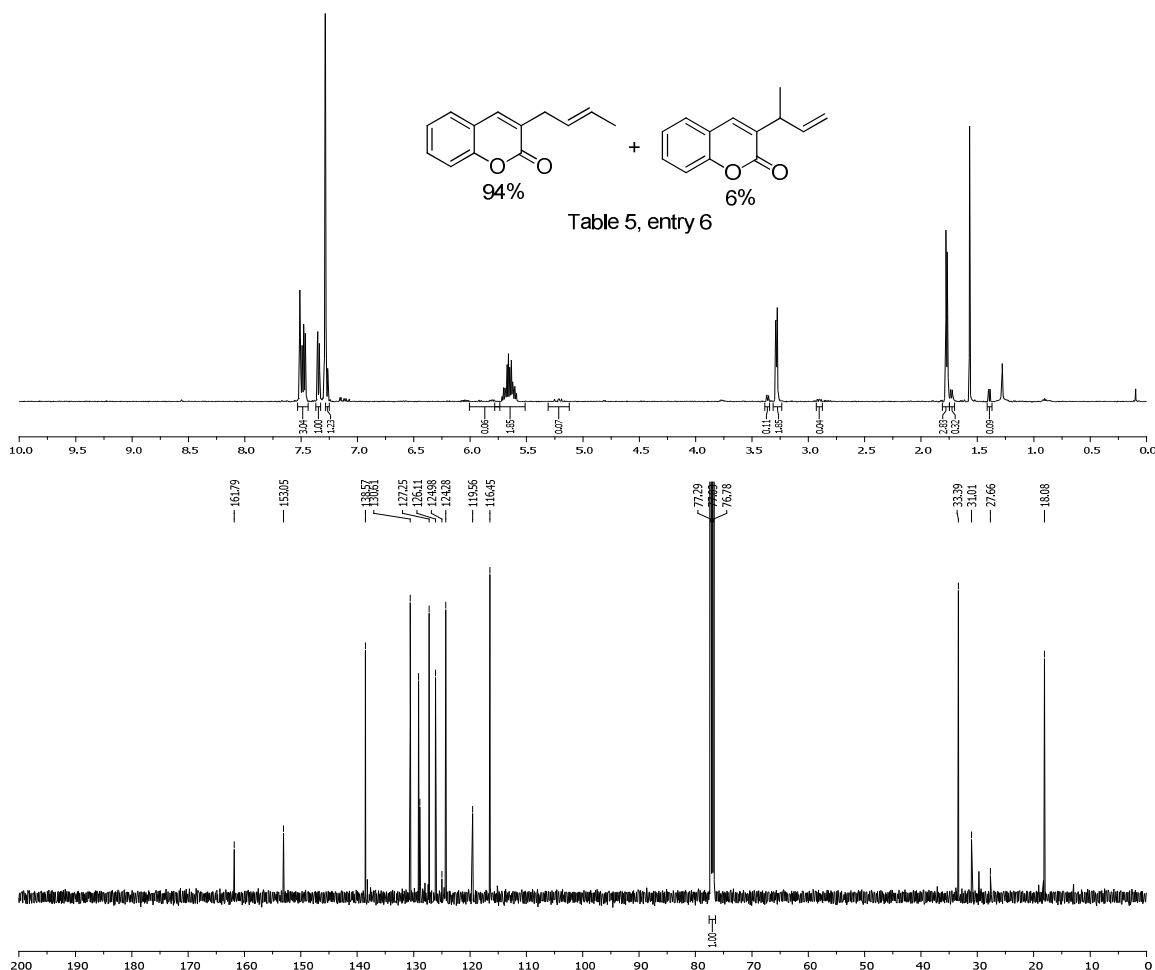
Colourless solid, m. p. 51 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 7.48 (t, *J* = 1.10 Hz, C4-H), 7.46 (dd, *J*₁ = 8.00 Hz, *J*₂ = 1.55 Hz, C5-H), 7.22 (dd, *J*₁ = 7.75 Hz, *J*₂ = 1.40 Hz, C7-H), 7.18 (dd, *J*₁ = *J*₂ = 7.7 Hz, C6-H), 4.96 (t, *J* = 1.60 Hz, CH₂-CH(CH₃)=CH), 4.86 (q, *J* = 1.10 Hz, CH(CH₃)=CH), 3.28 (s, CH₂-CH(CH₃)), 1.51 (s, C-CH₃); ¹³C NMR (126 MHz, CDCl₃) δ ppm 161.38 (C=O), 151.89 (Ar C, quat.), 142.00 (C(CH₃)=CH₂ quat.), 140.20 (C4-H), 137.68 (Ar C, quat.), 128.28 (Ar CH), 126.45 (Ar C, quat.), 125.75 (Ar CH), 123.81 (Ar CH), 119.89 (Ar C, quat.), 113.82 (C(CH₃)=CH₂), 38.00 (CH₂-C(CH₃)), 34.93 (C(CH₃)₃, quat.), 29.86 (C(CH₃)₃), 22.39 (C-CH₃); IR (CH₂Cl₂): ν 1720 (C=O), 1595 (C=C), 1436, 1164, 1058, 750 cm⁻¹; Calcd. HRMS for C₁₇H₂₁O₂ (M+H), 257.1542; Found, 257.1543.



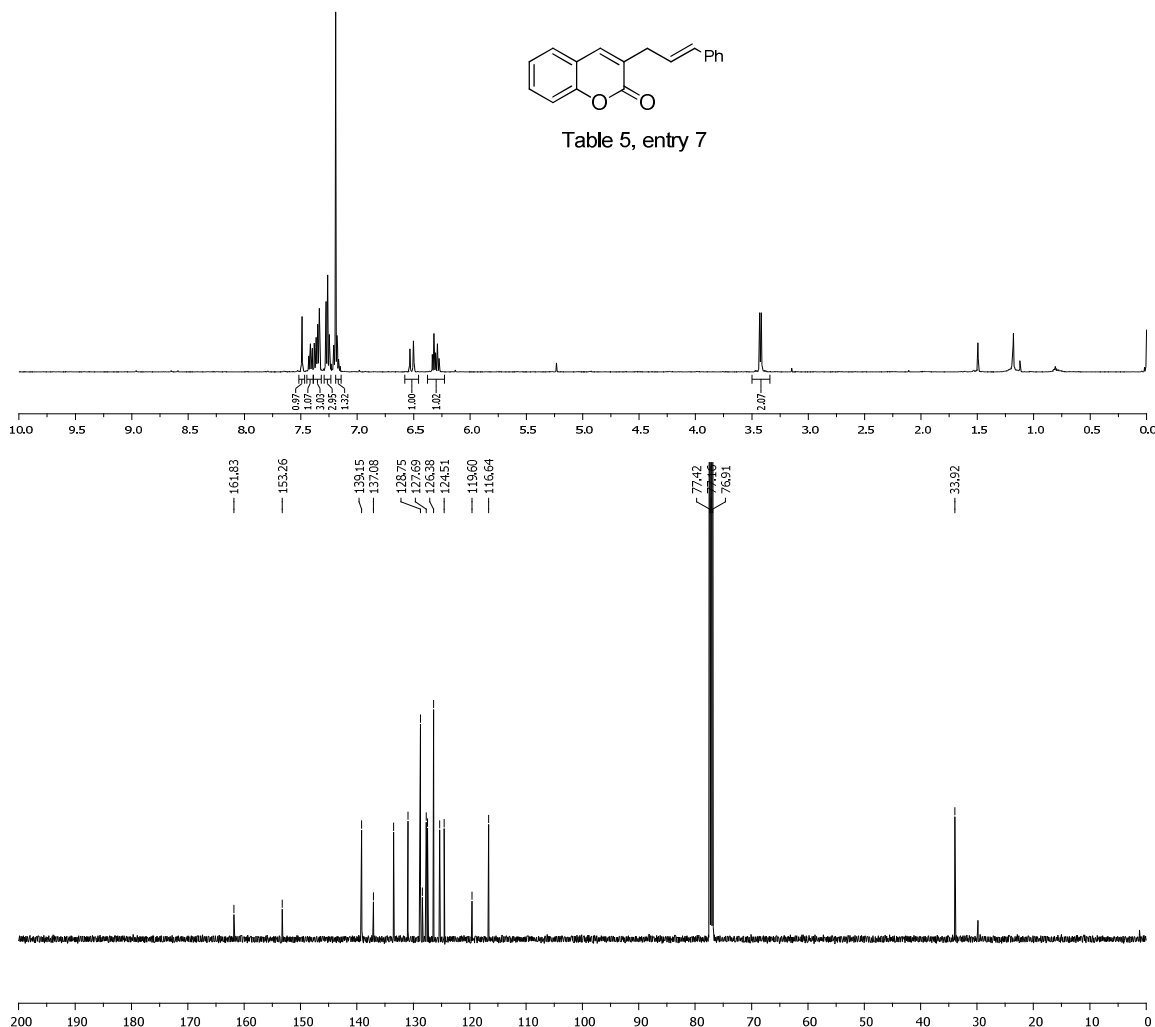
(*E*)-3-(Hex-2-enyl)-6-nitro-2H-chromen-2-one (Table 5, entry 4): Slight yellow solid, m. p. 108 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 8.39 (d, *J* = 2.65 Hz, C5-H), 8.33 (dd, *J*₁ = 9.10 Hz, *J*₂ = 2.65 Hz, C7-H), 7.55 (s, C4-H), 7.43 (d, *J* = 8.95 Hz, C8-H), 5.64-5.70 (m, CH₂-CH=CH-), 5.51-5.57 (m, -CH=CH-CH₂-CH₃), 3.29 (d, *J* = 6.80 Hz, -CH₂-CH=CH₂), 2.04-2.09 (m, =CH-CH₂-CH₂-), 1.40-1.47 (m, CH₂-CH₂-CH₃), 0.93 (t, *J* = 7.25 Hz, CH₂-CH₃); ¹³C NMR (126 MHz, CDCl₃) δ ppm 161.72 (C=O, quat.), 153.07 (C9, quat.), 143.99 (C6, quat.), 137.04 (C4-H), 135.65 (Ar CH), 131.73 (C3, quat.), 125.42 (CH₂-CH=CH-), 123.92 (CH=CH), 123.11 (Ar CH), 119.62 (Ar C, quat.), 117.55 (Ar CH), 34.66 (CH₂-CH=), 33.47 (=CH-CH₂), 22.61 (CH₂-CH₂-CH₃), 13.72 (CH₂-CH₃); IR (CH₂Cl₂): ν 1731 (C=O), 1635 (C=C), 1598 (C=C), 1529, 1342, 1271, 848, 746 cm⁻¹; Calcd. HRMS for C₁₅H₁₆NO₄ (M+H), 274.1079; Found, 274.1083.



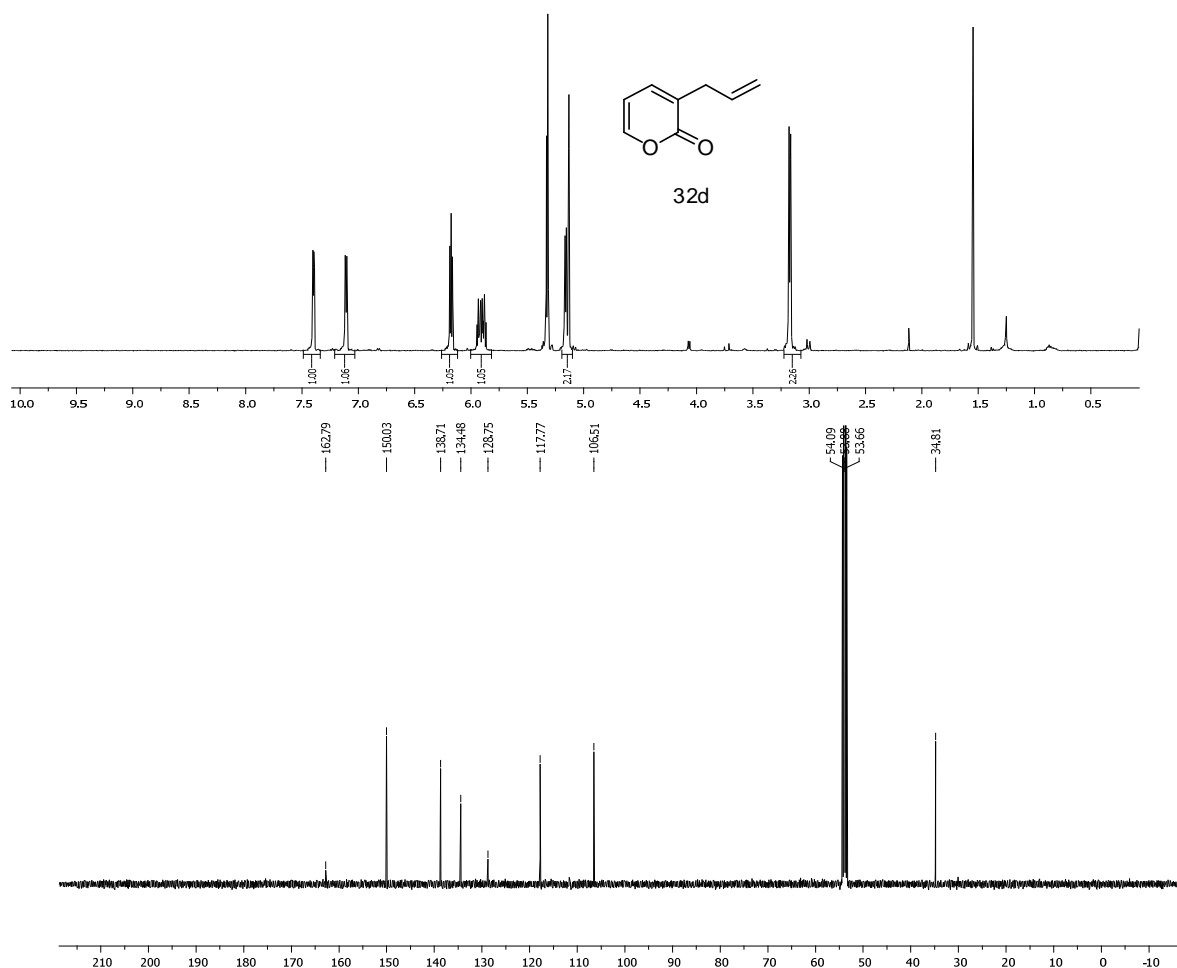
(*E*)-3-(Hex-2-enyl)-2H-chromen-2-one (Table 5, entry 5): Colorless solid, m. p. 63 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 7.48 (s, C4-H), 7.43-7.48 (m, 2Ar CH), 7.32 (d, *J* = 8.35 Hz, C5-H), 7.23-7.28 (m, Ar CH), 5.53-5.66 (CH₂-CH=CH-CH₂), 3.26 (d, *J* = 6.45 Hz, CH₂-CH), 2.03-2.08 (m, =CH-CH₂-CH₂-), 1.39-1.46 (m, CH₂-CH₂-CH₃), 0.92 (t, *J* = 7.40 Hz, CH₂-CH₃); ¹³C NMR (126 MHz, CDCl₃) δ ppm 161.72 (C=O, quat.), 153.07 (C9, quat.), 138.49 (C4-H), 134.51 (Ar CH), 130.57 (Ar CH), 129.03 (C3, quat.), 127.23 (CH₂-CH=CH-), 125.02 (CH=CH), 124.23 (Ar CH), 119.58 (Ar C, quat.), 116.44 (Ar CH), 34.67 (CH₂-CH=), 33.41 (=CH-CH₂), 22.48 (CH₂-CH₂-CH₃), 13.71 (CH₂-CH₃); IR (CH₂Cl₂): ν 1718 (C=O), 1631 (C=C), 1610 (C=C), 1456, 1170, 1051, 754 cm⁻¹; Calcd. HRMS for C₁₅H₁₆O₂Na (M+Na), 251.1048; Found, 251.1057.



(*E*)-3-(But-2-enyl)-2H-chromen-2-one (Table 5, entry 6): Highly viscous pale yellow liquid. (6% branched product was obtained). ^1H NMR (500 MHz, CDCl_3) δ ppm 7.51 (s, C4-H), 7.46-7.49 (m, 2Ar CH), 7.32 (d, $J = 8.20$ Hz, C5-H), 7.26-7.29 (m, Ar CH), 6.01-6.07 ($\text{CH}=\text{CH}$, branched), 5.59-5.71 ($-\text{CH}=\text{CH}-$), 5.18-5.25 (m, $=\text{CH}_2$), 3.28 (d, $J = 6.50$ Hz, $\text{CH}_2\text{-CH}$), 2.88-2.92 (m, $\text{CH}_2\text{-CH}$, branched), 1.76 (dd, $J_1 = 6.00$ Hz, $J_2 = 0.95$ Hz, $=\text{CH-CH}_3$), 1.39 (d, $J = 6.95$ Hz, $-\text{CH-CH}_3$, branched); ^{13}C NMR (126 MHz, CDCl_3) δ ppm 161.78 ($\text{C}=\text{O}$, quat.), 153.05 (C_9 , quat.), 138.57 ($\text{C}_4\text{-H}$), 130.61 (Ar CH), 129.12 (Ar CH), 128.91 (C_3 , quat.), 127.25 (Ar CH), 126.11 ($\text{CH}_2\text{-CH}=\text{CH}$), 124.28 ($\text{CH}=\text{CH-CH}_3$), 119.56 (Ar C, quat.), 116.45 (Ar CH), 33.39 ($\text{CH}_2\text{-CH}=\text{CH}_2$), 31.01 ($\text{CH}_3\text{-CH}$, branched), 18.08 ($\text{CH}_2\text{-CH}_3$); IR (CH_2Cl_2): ν 1718 ($\text{C}=\text{O}$), 1631 ($\text{C}=\text{C}$), 1610 ($\text{C}=\text{C}$), 1456, 1170, 1051, 754 cm^{-1} ; Calcd. HRMS for $\text{C}_{12}\text{H}_{13}\text{O}_2\text{Na}$ ($\text{M}+\text{Na}$), 223.0735; Found, 223.0741.

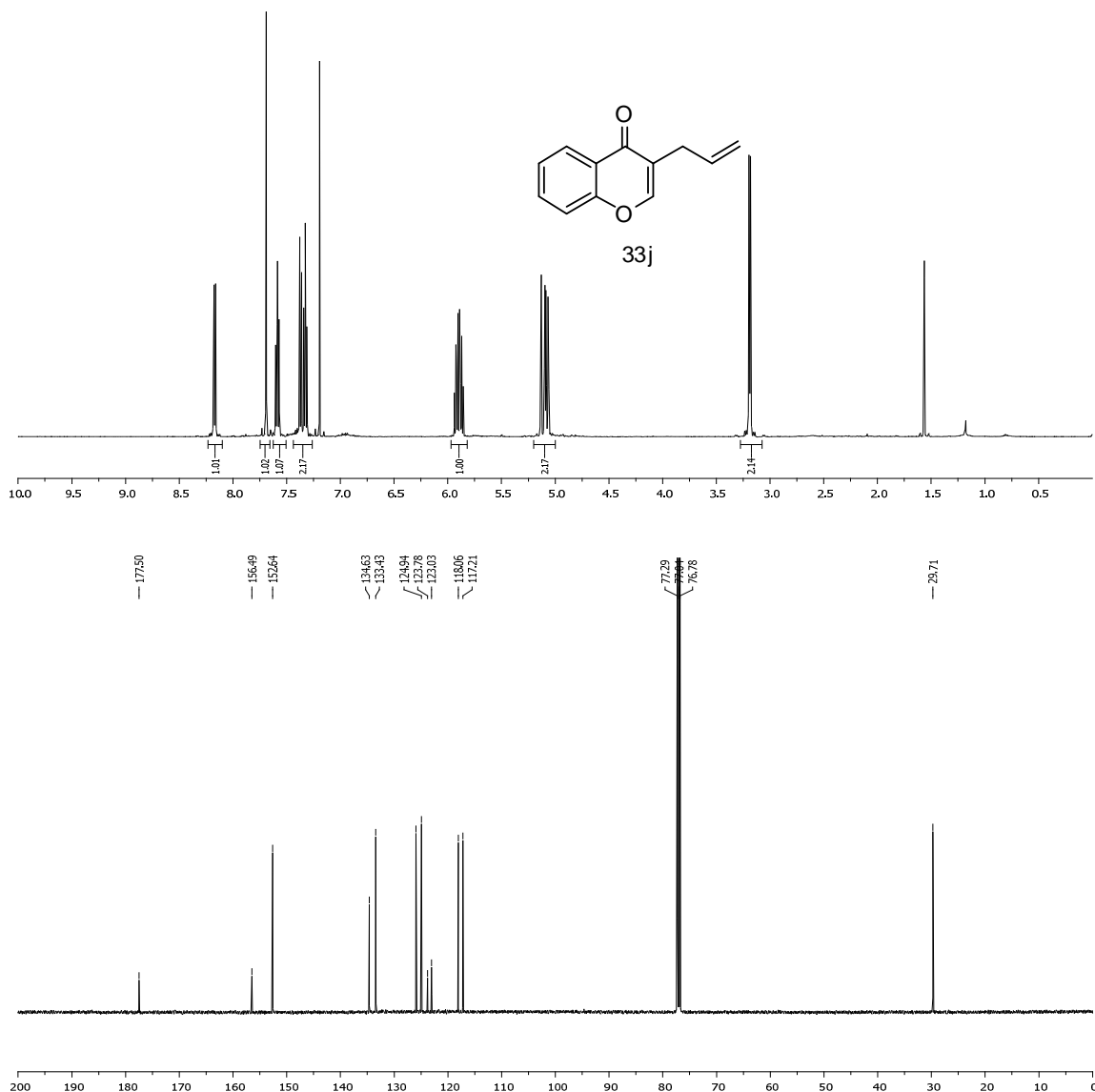


3-Cinnamyl-2H-chromen-2-one: Colourless solid, m. p. 110 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 7.56 (s, C5-H), 7.42-7.49 (m, 2Ar CH), 7.40 (s, C4-H), 7.31-7.35 (m, 3Ar CH), 7.23-7.28 (m, 2Ar CH), 6.58 (d, *J* = 15.9 Hz, CH=CH-CH₂), 6.34-6.40 (m, CH=CH-CH₂), 3.29 (d, *J* = 7.05 Hz, CH=CH-CH₂); ¹³C NMR (126 MHz, CDCl₃) δ ppm 161.83 (C=O, quat.), 153.26 (Ar C, quat.), 139.15 (C4-H), 137.08 (C3, quat.), 133.49 (CH=CH-Ph), 130.96 (Ar CH), 128.75 (2Ar CH), 128.40 (C3, quat.), 127.69 (Ar CH), 127.46 (Ar CH), 126.38 (2Ar CH), 125.32 (Ar CH), 124.51 (CH=CH-Ph), 119.60 (Ar C, quat.), 116.64 (Ar CH), 33.92 (CH₂-CH=); IR (CH₂Cl₂): ν 1714 (C=O), 1635 (C=C), 1605 (C=C), 1587, 1529, 1341, 1271, 848, 756 cm⁻¹; Calcd. HRMS for C₁₈H₁₅O₂ (M+H), 263.1072; Found, 274.1060.

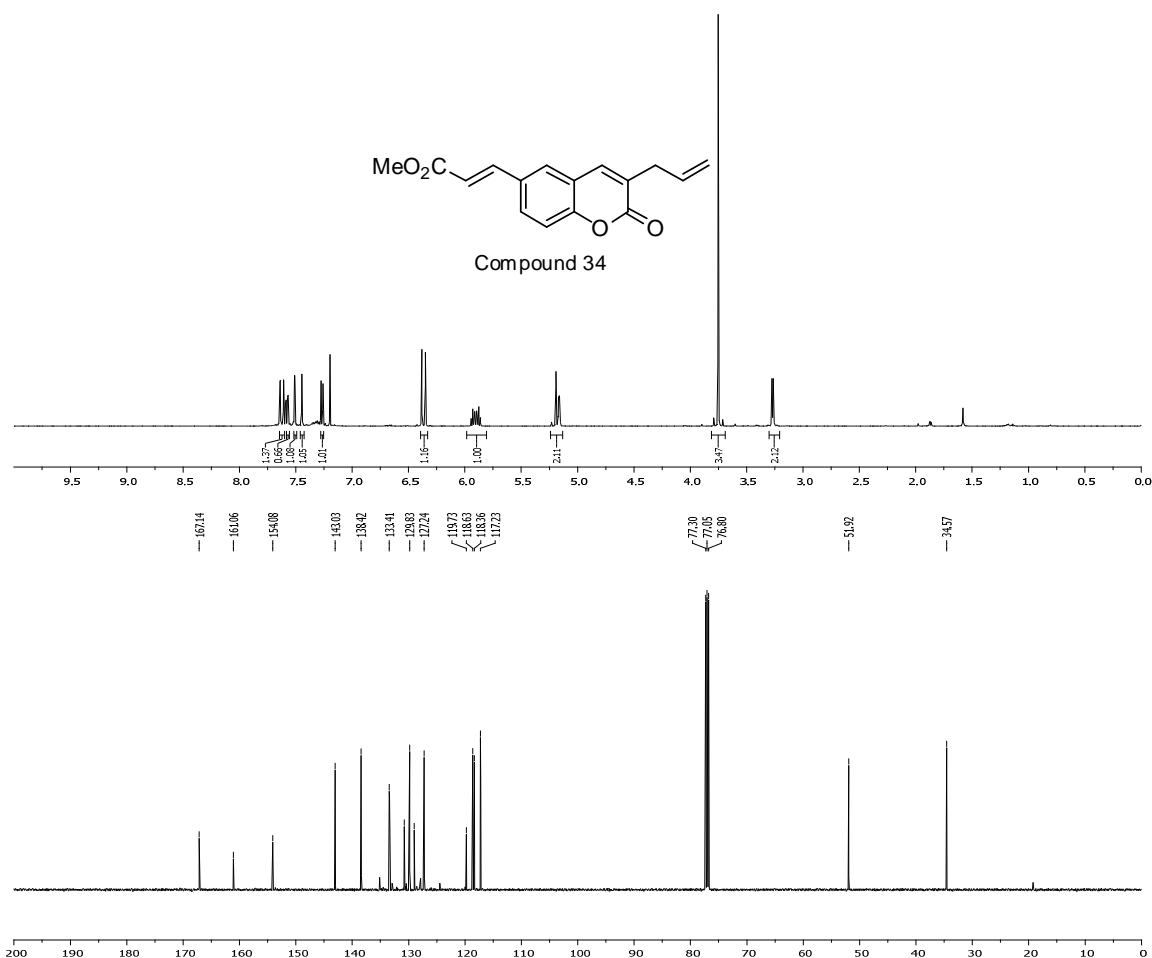


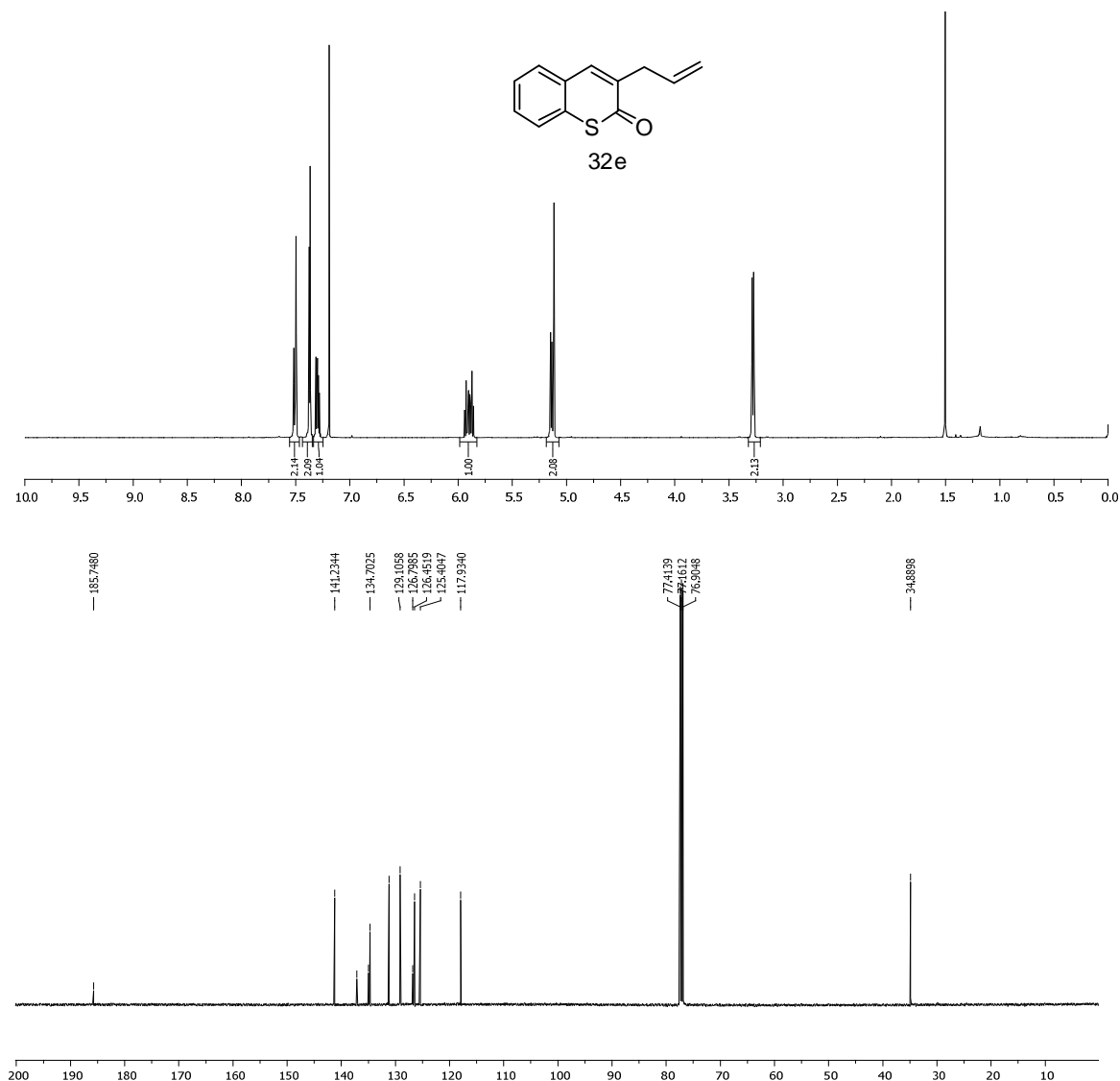
3-Allyl-2H-pyran-2-one (Compound 32d):²⁰ Colourless liquid, ¹H NMR (500 MHz, CD₂Cl₂) δ ppm 7.40 (dd, *J*₁ = 5.20 Hz, *J*₂ = 2.00 Hz, C6-H), 7.10 (d, *J* = 6.65 Hz, C4-H), 6.17 (dd, *J*₁ = 6.50 Hz, *J*₂ = 5.10 Hz, C5-H), 5.87-5.94 (m, CH₂-C=H), 5.14-5.17 (m, HC=CH₂), 3.17 (d, *J* = 6.80 Hz, CH₂-C=H); ¹³C NMR (126 MHz, CD₂Cl₂) δ ppm 162.78 (C=O, quat.), 150.03 (C6-H), 138.71 (C4-H), 134.47, (CH=CH₂), 128.74 (C3, quat.), 117.77 (CH=CH₂), 106.51 (C5-H), 34.81 (CH-CH₂); IR (CH₂Cl₂): ν 2968, 1725 (C=O), 1541 (C=C), 1477, 1147, 1136, 1046, 957 cm⁻¹; Calcd. HRMS for C₈H₈O₂ (M⁺), 136.0524; Found, 136.0523

²⁰ Posner, G. H.; Harrison, W.; Wettlaufer, D. G. *J. Org. Chem.* **1985**. 5041-5044.



3-Allyl-4H-chromen-4-one (Compound 33j): Colourless solid, m. p. 44 °C; ¹H NMR (500 MHz, CDCl₃) δ ppm 8.23 (dd, *J*₁ = 8.05 Hz, *J*₂ = 1.75 Hz, C5-H), 7.75 (t, *J* = 0.95 Hz, C2-H), 7.63-7.66 (m, Ar CH), 7.43 (dd, *J*₁ = 8.50 Hz, *J*₂ = 0.65 Hz, Ar CH), 7.37-7.40 (m, Ar CH), 5.92-6.00 (m, CH₂-C=H), 5.12-5.20 (m, HC=CH₂), 3.25 (dq, *J*₁ = 6.60 Hz, *J*₂ = 1.25 Hz, CH₂-C=H); ¹³C NMR (126 MHz, CDCl₃) δ ppm 177.50 (C=O), 156.48 (Ar C, quat.) 152.64 (C2), 134.63 (CH=CH₂), 133.43 (Ar CH), 125.93 (Ar CH), 124.94 (Ar CH), 123.78 (C3, quat.), 123.02 (Ar C, quat.), 118.05 (Ar CH), 117.20 (CH=CH₂), 29.71 (CH₂-C=H); IR (CH₂Cl₂): ν 2968, 1702 (C=O), 1531 (C=C), 1477, 1148, 1156, 1046, 951 cm⁻¹; Calcd. HRMS for C₁₂H₁₀O₂ (M⁺), 186.0681; Found, 186.0683.





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